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The evaluation of the Interlaboratory comparison Exercise for SO_2, CO, O_3, NO and NO_2 19.- 22. October 2009

Claudio A. Belis, Matej Kapus, Maurizio Barbiere and Friedrich Lagler

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Contact information
Address: via Fermi, 2749 T.P. 441, 21027 Ispra (VA), Italy
E-mail: claudio.belis@jrc.ec.europa.eu
Tel.: +39 0332 786644
Fax: +39 0332 785236

http://ies.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY

Executive Summary

From the 19th to the 22nd of October 2009 in Ispra (IT), 8 Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met at an interlaboratory comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, CO, NO, NO_2 and O_3).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

O the basis of criteria imposed by the European Commission, 85% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 14% of the results had good measured values, but the reported uncertainties were either too high (6%) or too small (8%).

The comparability of results among AQUILA participants is satisfactory for O_3, CO and NO measurement methods. This is not the case for SO_2 and NO_2 which comparability in the present exercise is not satisfactory with respect to the settled quality criteria.

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Abbreviations:

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas phase titration
IE	Intercomparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	the oxides of nitrogen, the sum of NO and NO_2
NRL	National Reference Laboratory
O_3	Ozone
SO_2	Sulphur dioxide
WHO CC-EURO	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols:

symbol	*explanation*
α	converter efficiency (EN 14211; [4])
E_n	E_n – number statistic (ISO 13528; [13])
r	repeatability limit (ISO 5725; [14])
R	reproducibility limit (ISO 5725; [14])
σ_p	standard deviation for proficiency assessment (ISO 13528; [13])
x*	robust average (Annex C ISO 13528; [13])
s*	robust standard deviation (Annex C ISO 13528; [13])
s_r	repeatability standard deviation (ISO 5725; [14])
s_R	reproducibility standard deviation (ISO 5725; [14])
U_X	expanded uncertainty of the assigned/reference value (ISO 13528; [13])
U_{xi}	expanded uncertainty of the participant's value
u_X	standard uncertainty of the assigned/reference value (ISO 13528; [13])
X	assigned/reference value (ISO 13528; [13])
x_i	average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [14])
$x_{i,j}$	j-th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [14])
z'	z'-score statistic (ISO 13528; [13])

1. Introduction

As a result of the revision of the legislation framework on air quality in the CAFÉ (Clean Air for Europe) thematic strategy, former mother and most daughter directives were integrated and systematized into a single rule. With the adoption of Directive 2008/50/EC [1] on ambient air quality and cleaner air for Europe, a framework for a harmonized air quality assessment in Europe was set. One important objective of the Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O_3). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods for CO [2], SO_2 [3], NO-NO_2 [4] and O_3 [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Air Quality Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC) organizes interlaboratory comparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [9] [10], but with a view to obtaining harmonized air quality data for health related studies. Their program integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimize resources and have better international harmonization. The following report deals with the IE that took place from 19^{th} to the 22^{nd} of October 2009 in Ispra (IT) in joint cooperation of EC/ JRC/IES/ERLAP and WHO CC.

Since 1990 ERLAP organises IEs aiming at evaluating the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories. Currently, a more systematic approach has been adopted, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [11], aiming both at providing an alert mechanism for the purposes of the EC legislation and at supporting the implementation of quality schemes by NRLs. The methodology for the organization of IEs was developed by ERLAP in collaboration with AQUILA and is described in a position paper on the organization of intercomparison exercises for gaseous air pollutants [12].
This evaluation scheme was adopted in December 2008 and is applied to all IEs since then. It contains common criteria to alert the EC on possible performance failures which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z'-score method [13] with the uncertainty requirements for calibration gases stated in the European standards [2], [3], [4] and [5], which are consistent with the DQOs of European Directives.
According to the said document, NRLs with an overall unsatisfactory performance in the z'-score evaluation (one unsatisfactory or two questionable results per parameter) ought to repeat their participation in the following IE in order to demonstrate remediation measures [12]. In addition,

considering that the evaluation scheme should be useful to participants for accreditation according to ISO 17025, they are requested to include their measurement uncertainty. Hence, participants' results (measurement values and uncertainties) are compared to the assigned values applying the E_n – number method [13].

Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardized measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different IEs.

2. Communication and time schedule

The IE was announced in May 2009 to the members of the AQUILA network and the WHO CC representative. A registration letter was send to interested parties and the registration was closed in September 2009 with the list of 8 participating laboratories.
The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Monday, 19^{th} October 2009, for the installation of their equipment. The calibration of NOx and O_3 analysers was carried out on Tuesday morning and the generation of NOx and O_3 gas mixtures started at 11:00. The calibration of SO_2 and CO analysers was carried out on Wednesday 18:00 and the generation of CO and SO_2 gas mixtures started at 20:00. The test gases generation finished on Thursday at 8:30.

3. Participants

All participants were organizations dealing with the routine ambient air monitoring or health related studies. The national representatives came from EU member states, United Kingdom, Slovenia, Estonia, Hungary, Spain and Denmark, and from non EU member states Croatia and Serbia..

Country	Laboratory	Code
United Kingdom	AEA Technology	A
Slovenia	Environmental Agency of the Republic of Slovenia	B
European Commission	European Reference Laboratory for Air Pollution	C
Estonia	Estonian Environmental Research Centre	D
Croatia	Energy and Environmental Protection Institute	E
Hungary	Hungarian Meteorological Service	F
Serbia	Institute of Public Health of Belgrade	G
Spain	Health Institute CARLOS III	H
Denmark	National Environmental Research Institute	I

Table 1: The list of participating organizations.

In Table 2 are reported the manufacturer and model of the instrumentation used by every participant during the interlaobratory comparison exercise included those used in the calculation of the assigned values. As a whole, the instrumentation belongs to three different manufacturers with the exception of SO_2 where are present four brands. The list contains the information reported by participants and by no means can be considered as an implicit or explicit endorsement of the organizers to any specific type of instrumentation. This information is made available with the only purpose of making it possible to track the performance of the different models and type approvals and to evaluate their influence on the quality of the measurements. Nevertheless, the above-mentioned evaluation is beyond the scope of the present report.

Gas	Lab Code	Instrument
CO	A	Teledyne API 300E
	B	Horiba APMA 360 CE
	C	Thermo Electronic Corporation 48C
	D	Horiba APMA 360
	E	Horiba APMA 370
	F	Thermo Electronic Corporation 48C
	G	Horiba APMA 360
	H	Thermo Electronic Corporation 48C
	I	Teledyne API 300
NO_X	A	Teledyne API 200E
	B	Horiba APNA 360 CE
	C	Thermo Electrom Corporation 42C
	D	Horiba APNA 360
	E	Horiba APNA 370
	F	Thermo Electrom Corporation 42C
	G	Horiba APNA 360
	H	Thermo Electrom Corporation 42i
	I	Teledyne API 200A
O_3	A	Teledyne API 400E
	B	Thermo Electronic Corporation 49C
	C	Thermo Electronic Corporation 49C
	D	Horiba APOA 360
	E	Horiba APOA 370
	F	Thermo Electronic Corporation 49C
	G	Horiba APOA 360
	H	Teledyne API 400E
	I	Teledyne API 400A
SO_2	A	Teledyne API 100A
	B	Horiba APSA 360 A
	C	Thermo Electrom Corporation 43C
	D	Horiba APSA 360
	E	Horiba APSA 370
	F	Thermo Electrom Corporation 43C
	G	Horiba APSA 360
	H	Environment AF22M
	I	Teledyne API 100E

Table 2: The list of instruments used by participants

4. The preparation of test mixtures

The ERLAP IE facility has been described in several reports [17] and [18]. During this IE, gas mixtures were prepared for SO_2, CO, O_3, NO and NO_2 at concentration levels around limit values, critical levels and assessment thresholds set by European Air Quality Directive [1].

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, SO_2 or CO using thermal mass flow controllers [8]. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration method [19] in a condition of NO excess.

The participants were required to report three half-hour-mean measurements for each concentration level (run) in order to evaluate the repeatability of standardized measurement methods. Zero concentration levels were generated for one hour and one half-hour-mean measurement was reported. The sequence program of generated test gases is given in Table 3.

day	start time	duration	operation or run number	zero air	NO	NO_2	O_3	CO	SO_2
		(h)		(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(μmol/mol)	(nmol/mol)
19-Oct	12:00	6	installation						
20-Oct	8:00	3	calibration						
20-Oct	11:00	1	NO & NO_2 & O_3 run 0	0					
20-Oct	12:00	2	NO & NO_2 run 1		500	0			
20-Oct	14:00	2	NO & NO_2 run 2		380	120			
20-Oct	16:00	2	O_3 run 1				120		
20-Oct	18:00	2	NO & NO_2 run 3		250	0			
20-Oct	20:00	2	NO & NO_2 run 4		146	104			
20-Oct	22:00	2	O_3 run 2				104		
21-Oct	0:00	2	NO & NO_2 run 5		150	0			
21-Oct	2:00	2	NO & NO_2 run 6		90	60			
21-Oct	4:00	2	O_3 run 3				60		
21-Oct	6:00	2	NO & NO_2 run 7		50	0			
21-Oct	8:00	2	NO & NO_2 run 8		29	21			
21-Oct	10:00	2	O_3 run 4				21		
21-Oct	12:00	2	NO & NO_2 run 9		16	0			
21-Oct	14:00	2	NO & NO_2 run 10		2	14			
21-Oct	16:00	2	O_3 run 5				14		
21-Oct	< 18:00	2	calibration						
21-Oct	20:00	1	CO & SO_2 run 0	0					
21-Oct	21:00	2:30	CO & SO_2 run 1					9	132
21-Oct	23:30	2	CO & SO_2 run 2					6	47
22-Oct	1:30	2	CO & SO_2 run 3					4	19
22-Oct	3:30	2	CO & SO_2 run 4					2	8
22-Oct	5:30	2	CO & SO_2 run 5					1	3
22-Oct	7:30	1		0					
22-Oct	8:30				END				

Table 3: The sequence program of generated test gases

5. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 [13] was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole IE [12]. The traceability of ERLAP's measurement results and the method applied to validate them are presented in Annex A. In the following proficiency evaluations, the uncertainty of test gas homogeneity (Annex A) was added to the uncertainties of ERLAP's measurement results.

All data reported by participating laboratories are presented in Annex B.

As it is described in the said position paper [12], the proficiency of the participants was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests whether the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion. The second performance indicator (E_n-number) tests if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participants measurement result and the uncertainty of the assigned/reference value.

5.1 z' - score

The z'- score statistic is calculated according to ISO 13528 [13] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_X^2}} \qquad (1)$$

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_X' is the standard uncertainty of assigned value. For 'a' and 'b' see Table 4.

In the European standards [1], [3], [4] and [5] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p is calculated by linear interpolation between 2.5% at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous IEs. The linear function parameters of σ_p are given in Table 4:

	σ_p=a·c+b	
Gas	**a**	**b** nmol/mol
SO_2	0.022	1
CO	0.024	100
O_3	0.020	1
NO	0.024	1
NO_2	0.020	1

Table 4: The standard deviation for proficiency assessment
It is a linear function of concentration (c) with parameters: slope (a) and intercept (b).

The assessment of results in the z‘-score evaluation is made according to the following criteria:

- $|z'| \leq 2$ are considered satisfactory.
- $2 < |z'| \leq 3$ are considered questionable.
- $|z'| > 3$ are considered unsatisfactory. Scores falling in this range are very unusual and are taken as evidence that an anomaly has occurred that should be investigated and corrected.

The results of z’-score evaluation are presented in bar plots (Figure 1 to Figure 5) in which the z’-scores of each participant are grouped together, and assessment criteria are presented as z’=±2 and z’=±3 lines.

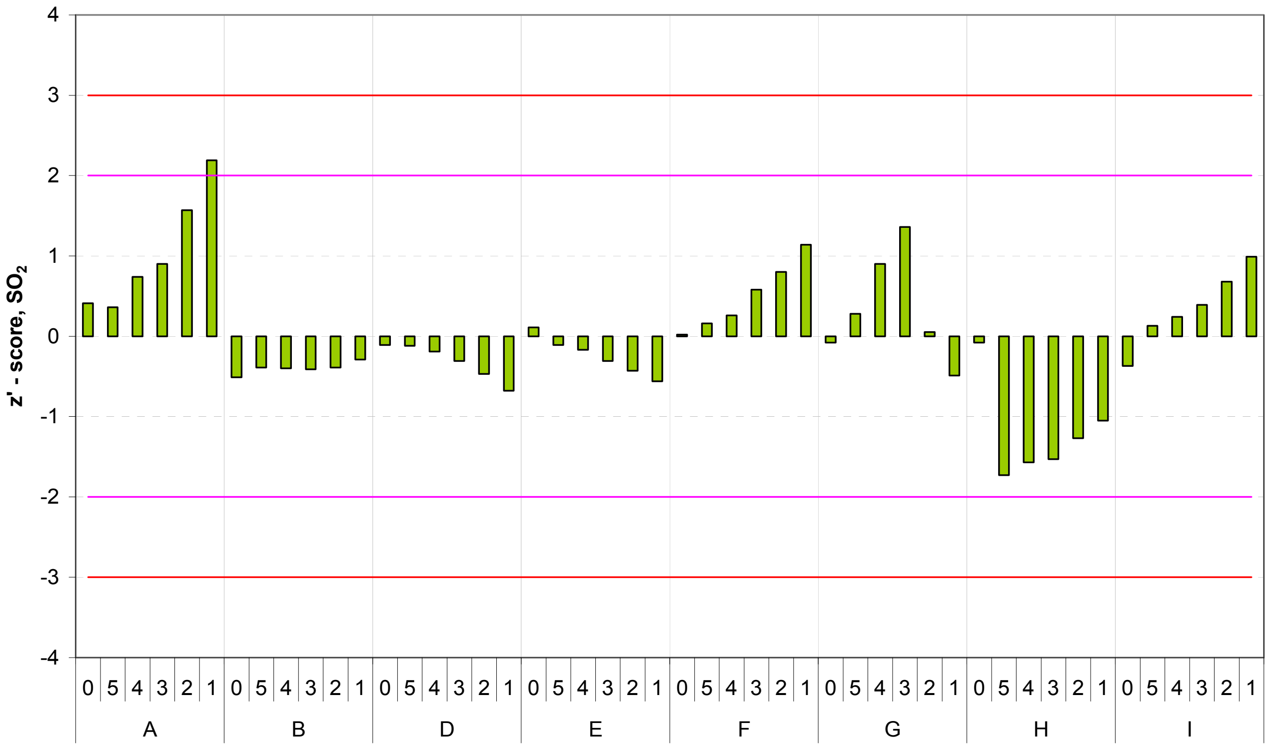

Figure 1: The z’-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). The evaluations are in the order of increasing concentrations. Run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (3 nmol/mol), 4 (8 nmol/mol), 3 (19 nmol/mol), 2 (47 nmol/mol), 1 (132 nmol/mol). The assessment criteria are presented as z’=±2 and z’=±3 lines. They represent the limits for the questionable and unsatisfactory results.

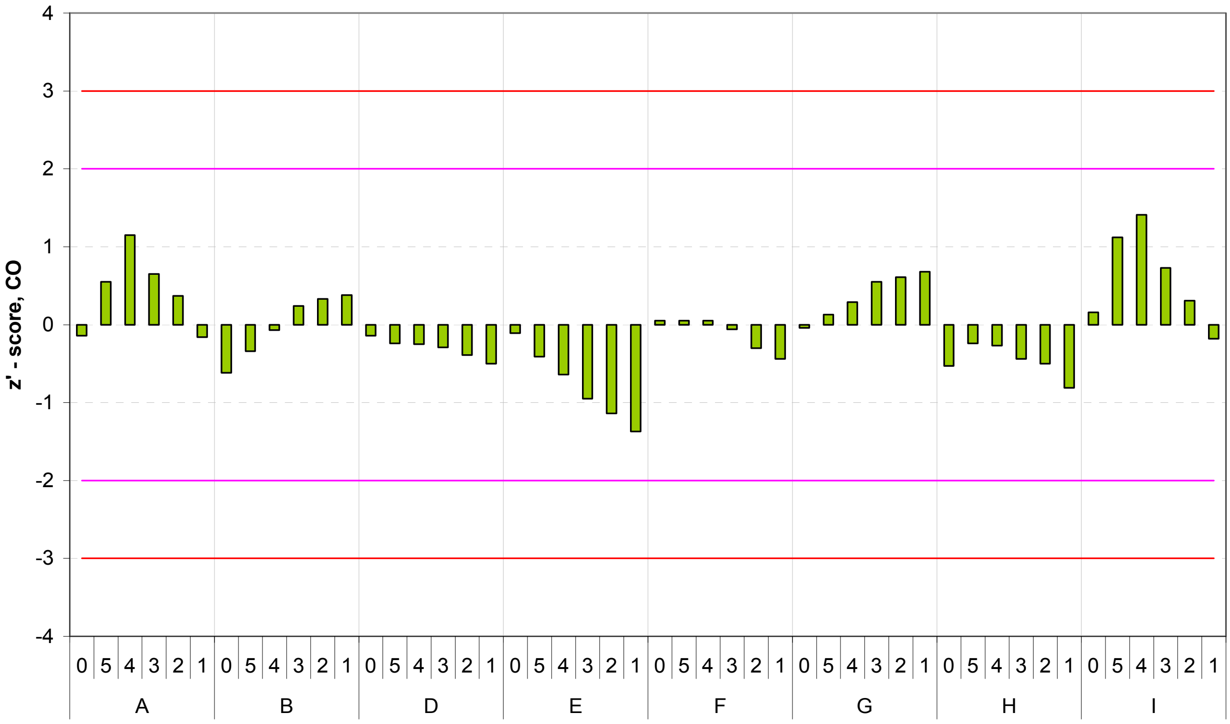

Figure 2: The z'-score evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). The evaluations are in the order of increasing concentrations. Run number order (with nominal concentration) is: 0 (0 µmol/mol), 5 (1 µmol/mol), 4 (2 µmol/mol), 3 (4 µmol/mol), 2 (6 µmol/mol), 1 (9 µmol/mol). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

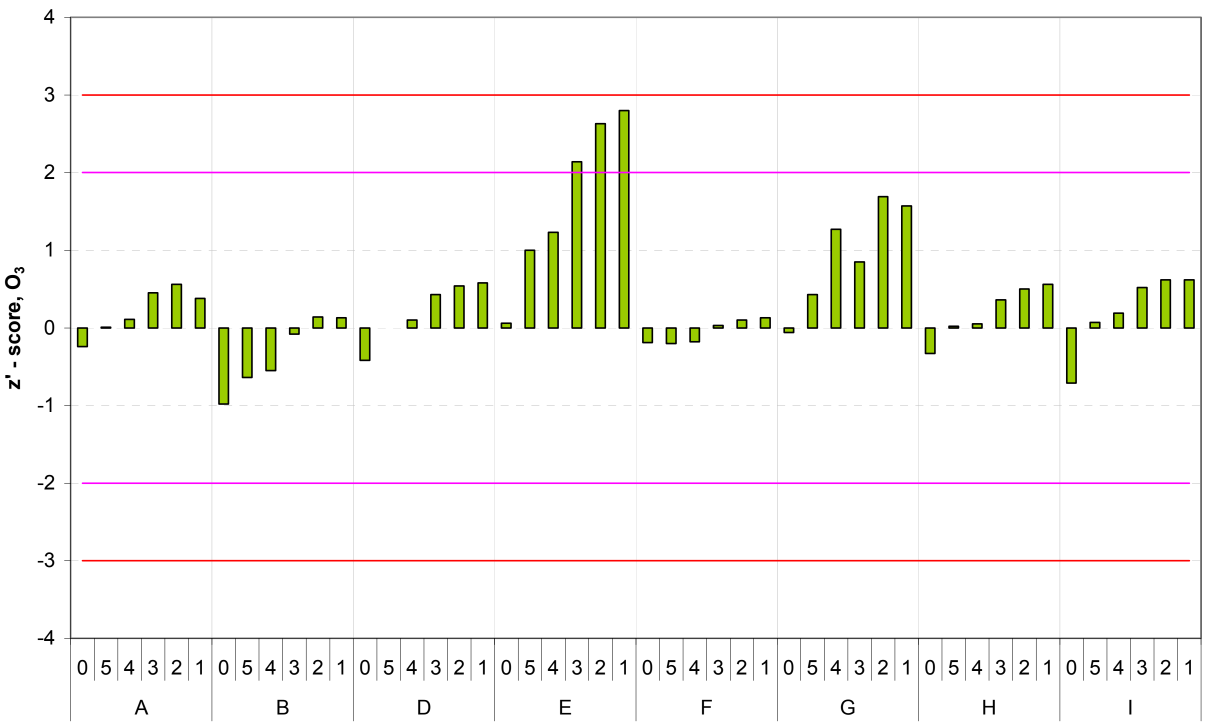

Figure 3: The z'-score evaluations of O_3 measurements
Scores are given for each participant and each concentration level (run). The evaluations are in the order of increasing concentrations. Run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (14 nmol/mol), 4 (21 nmol/mol), 3 (60 nmol/mol), 2 (104 nmol/mol), 1 (120 nmol/mol) The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

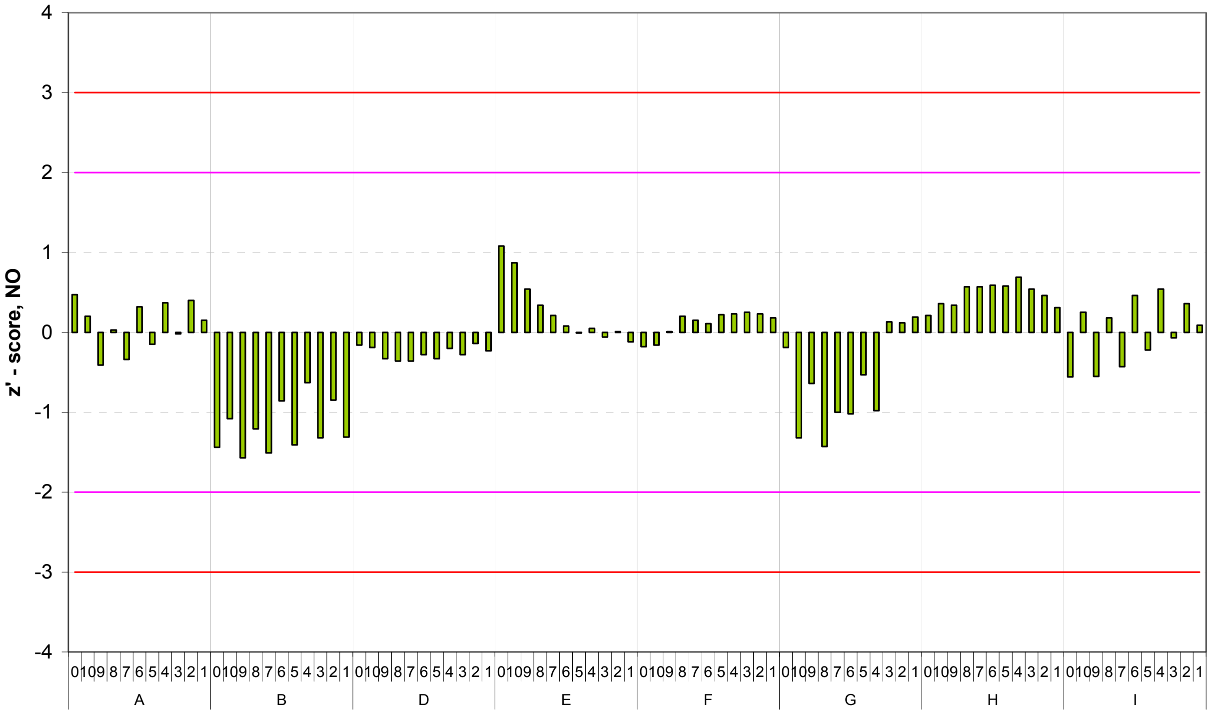

Figure 4: The z'-score evaluations of NO measurements
Scores are given for each participant and each tested concentration level (run). The evaluations are in the order of increasing concentrations. Run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (29 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (146 nmol/mol) , 3 (250 nmol/mol) , 2 (380 nmol/mol), 1 (500 nmol/mol). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

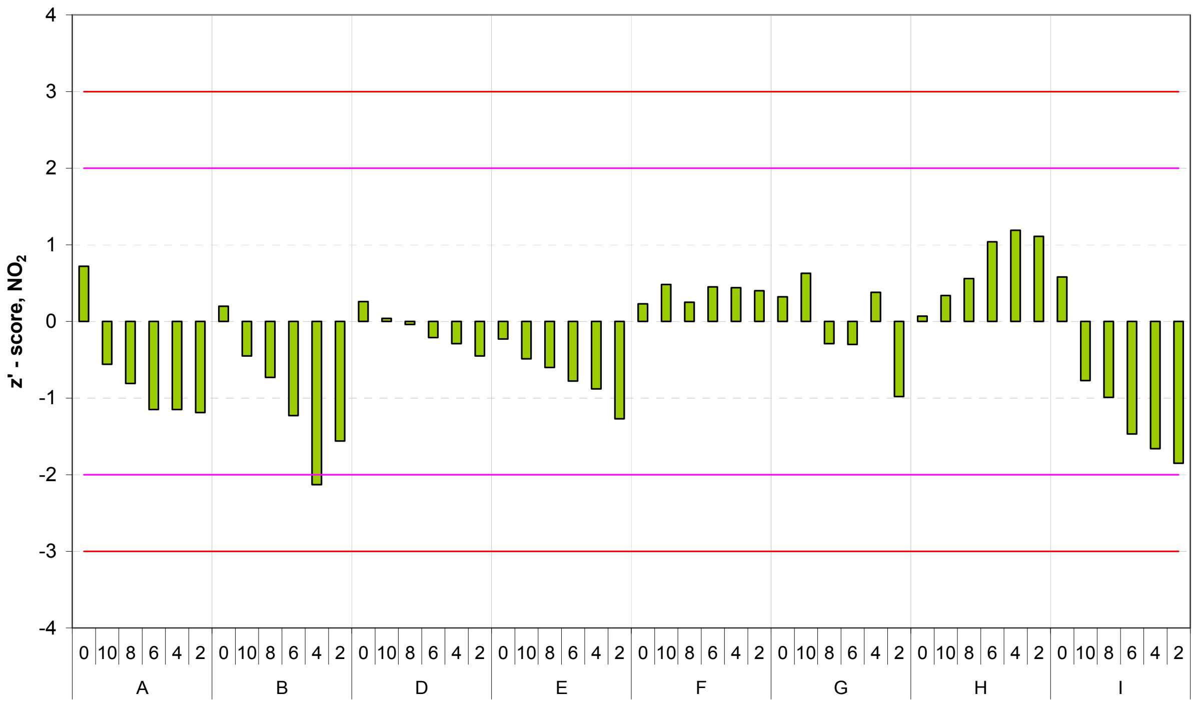

Figure 5: The z'-score evaluations of NO_2 measurements
Scores are given for each participant and each concentration level (run). The evaluations are in the order of increasing concentrations. Run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (14 nmol/mol), 8 (21 nmol/mol), 6 (60 nmol/mol), 4 (104 nmol/mol), 2 (120 nmol/mol). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

5.2 E_n - number

The normalised deviations [13] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}} \qquad (2)$$

where 'X' is the assigned/reference value with an expanded uncertainty 'U_X' and 'x_i' is the participant's average value with an expanded uncertainty 'U_{Xi}'. Satisfactory results are the ones for which $|E_n| \leq 1$.

In Figure 6 to Figure 10 the biases of each participant (x_i-X) are plotted and error bars are used to denote the value of denominator of equation $2\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 4) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

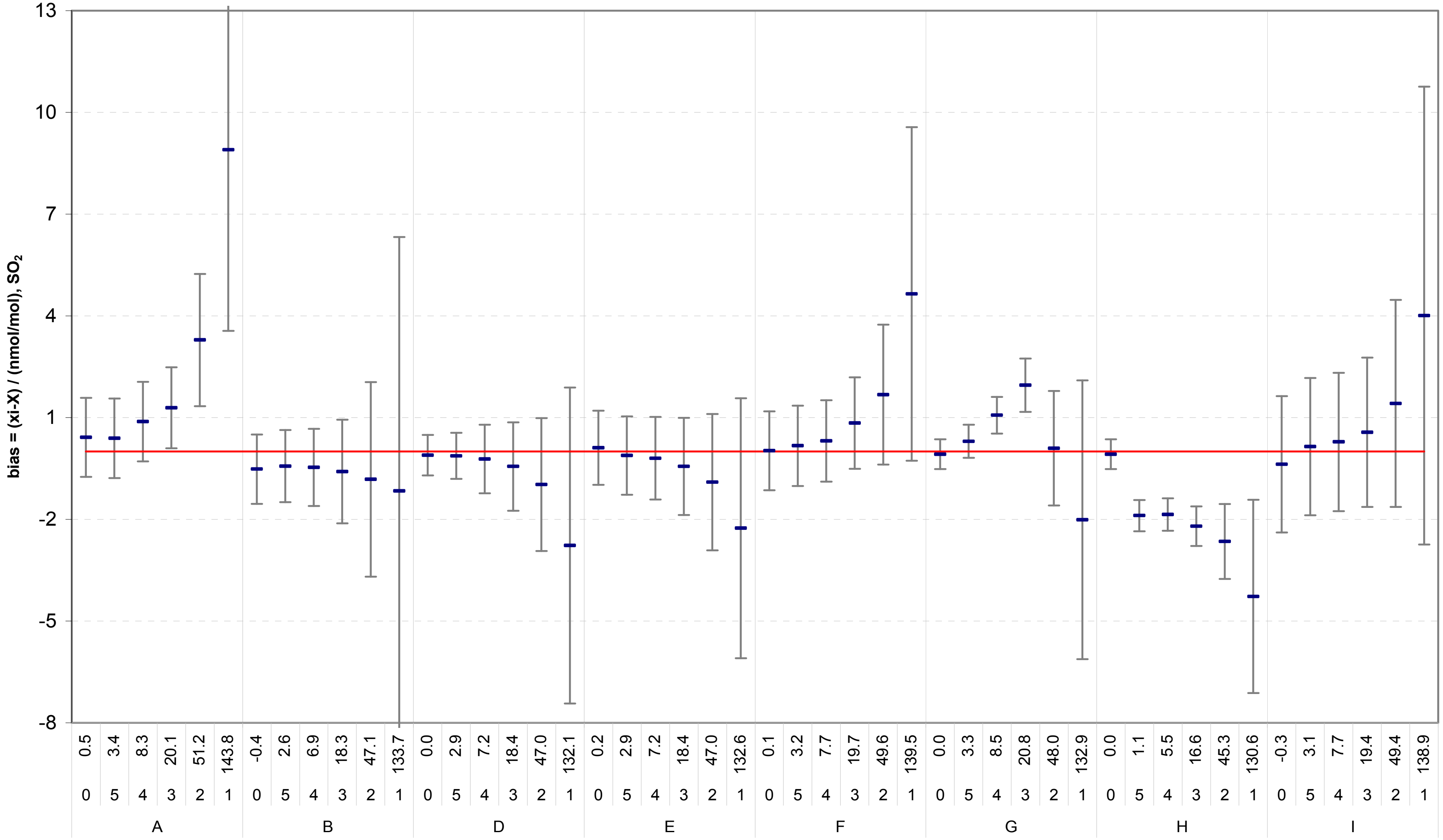

Figure 6: Bias of participant's SO_2 measurement results
Expanded uncertainty of bias for each run is presented as error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

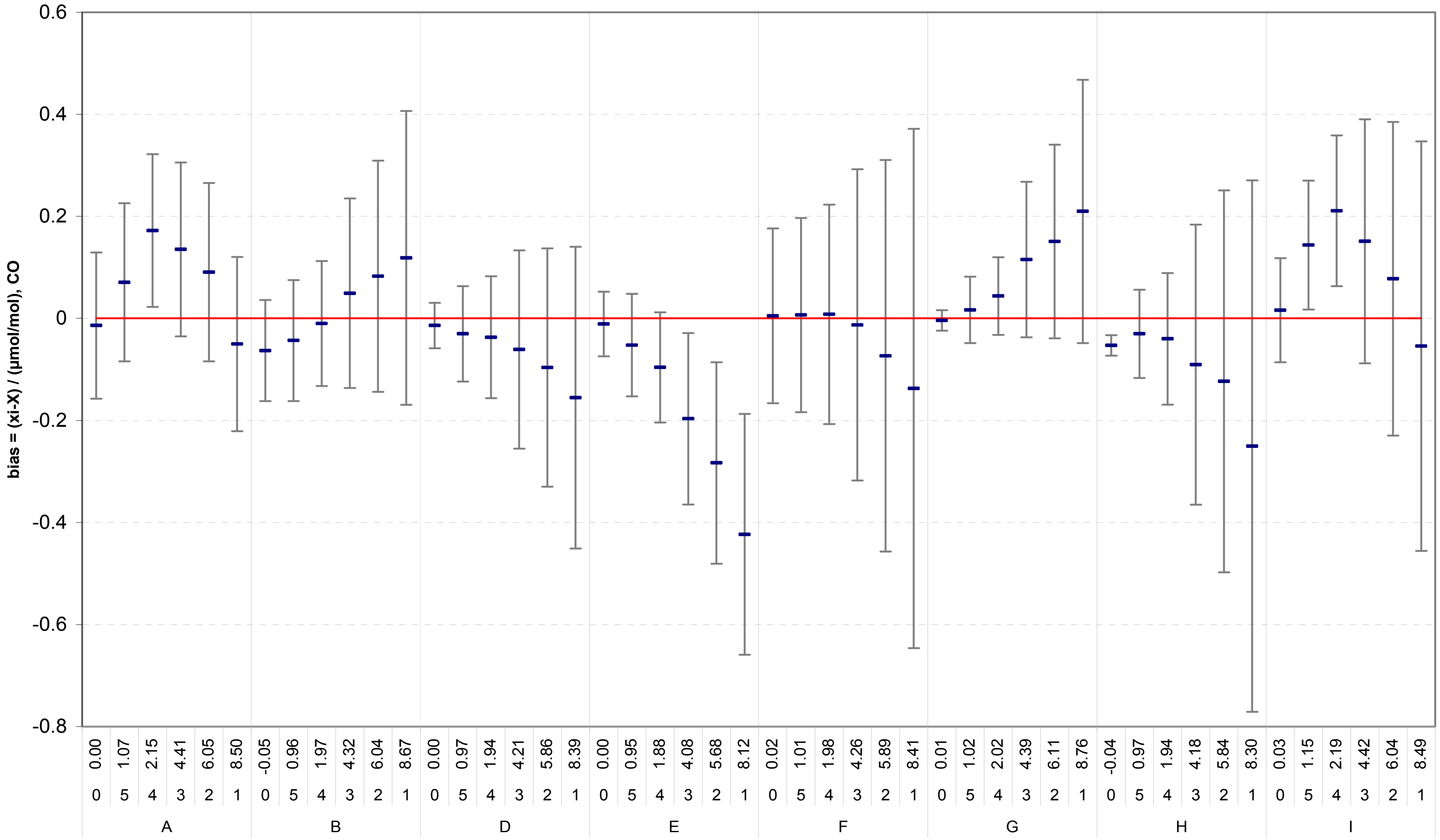

Figure 7: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (µmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

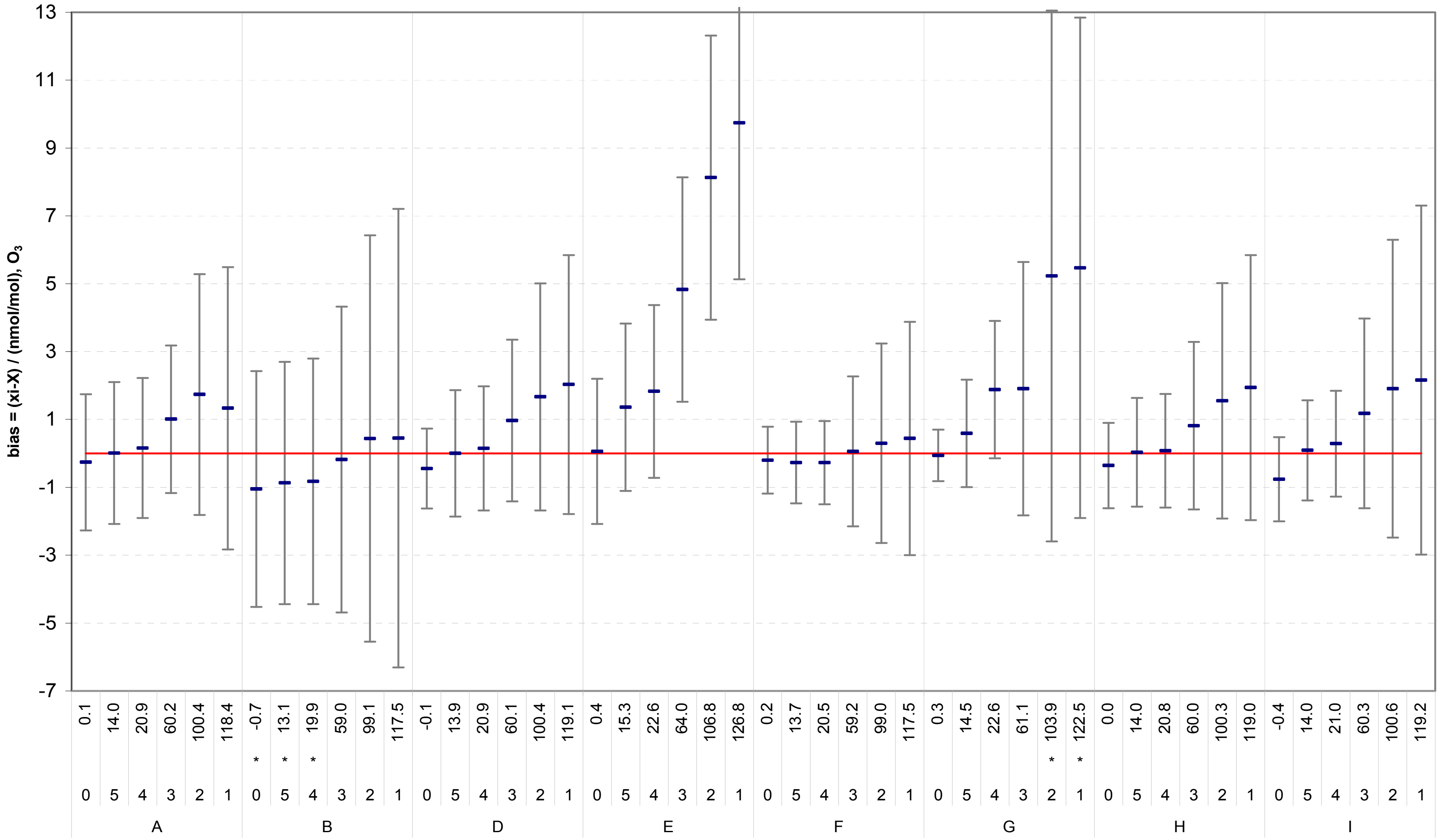

Figure 8: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

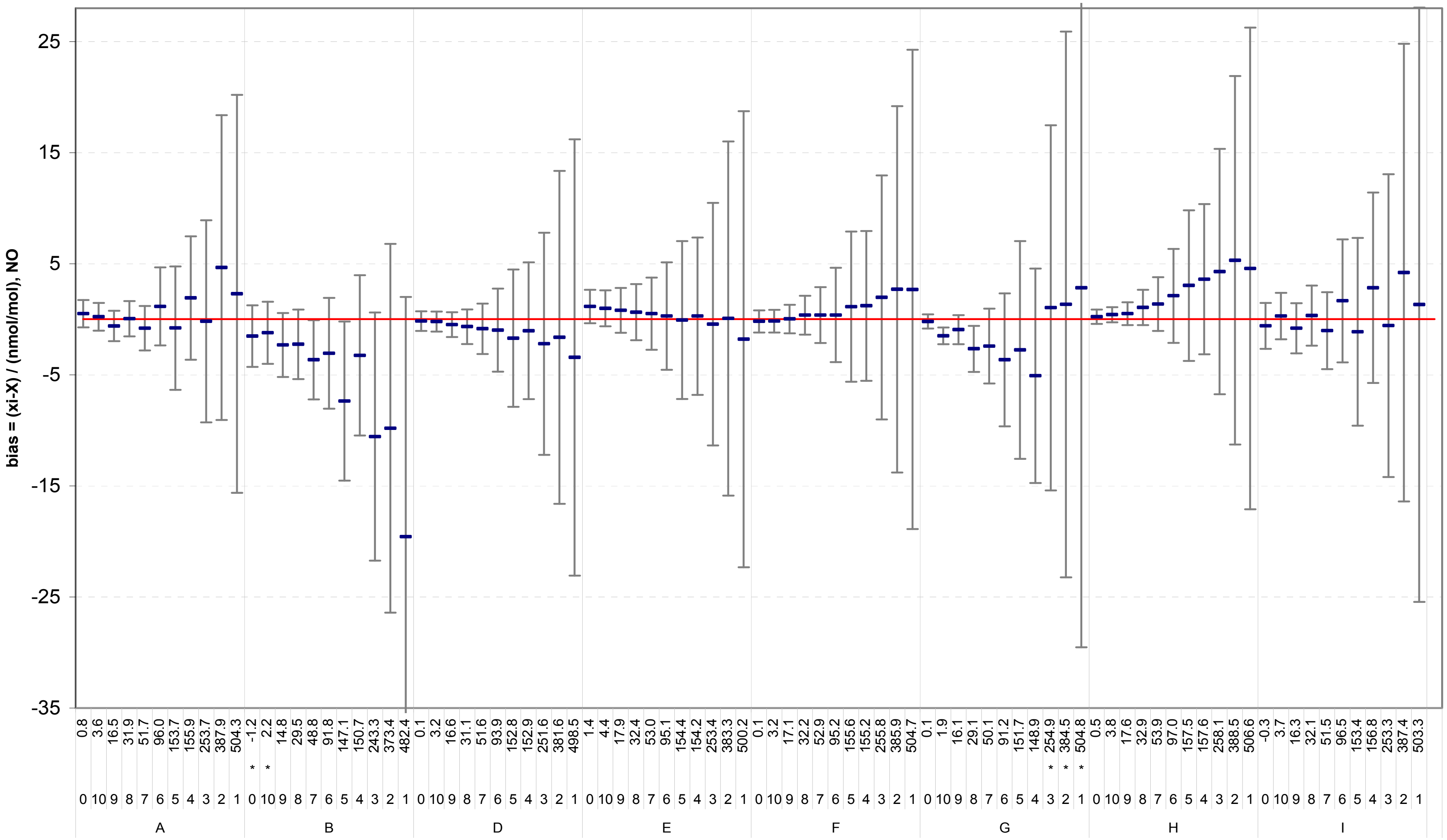

Figure 9: Bias of participant's NO measurement results

Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σp.

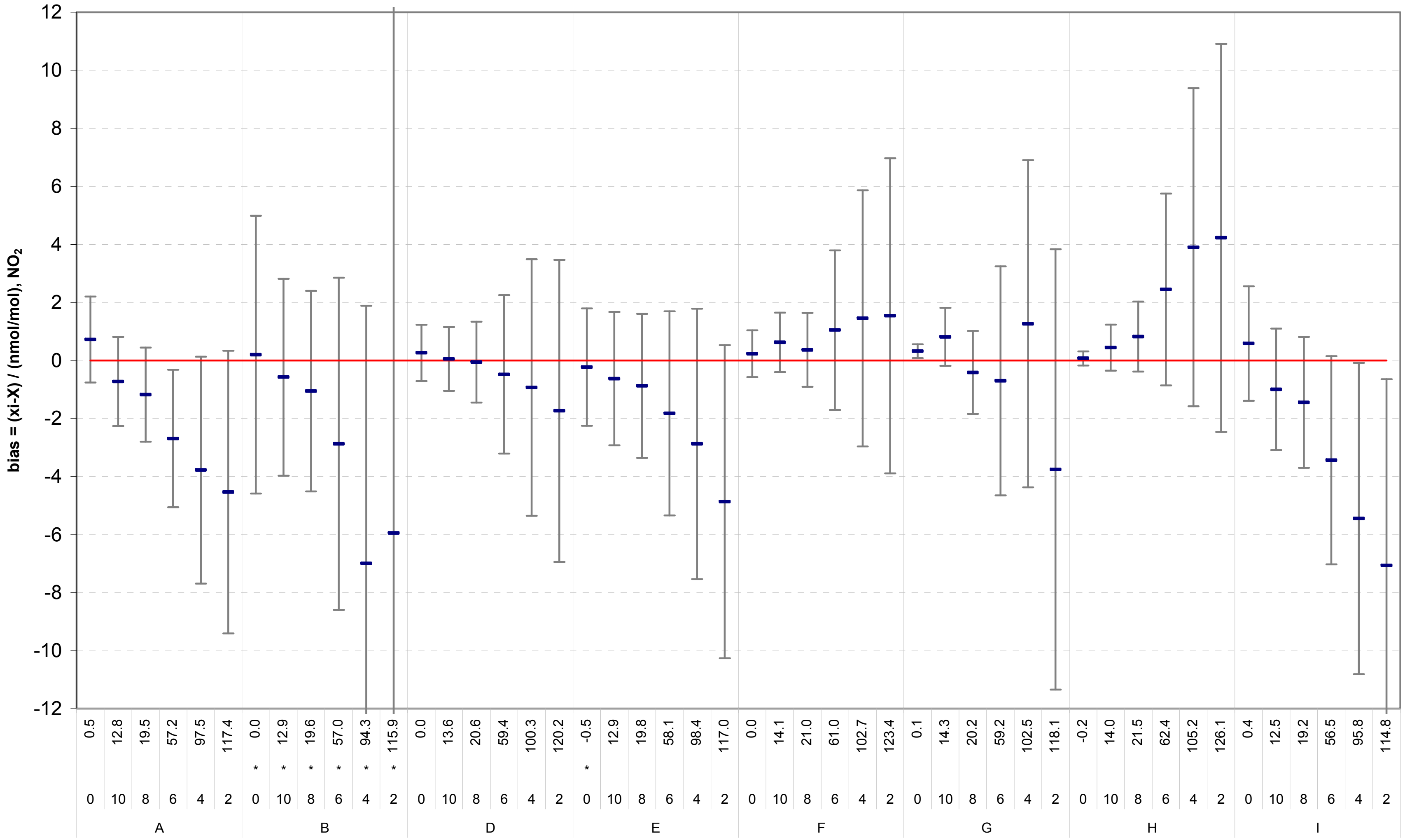

Figure 10: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

6. *Performance characteristics of individual laboratories*

Individual participants' biases were evaluated and are presented in chapter 5 (Figure 6-Figure 10). Since the results of NO_2 runs 1, 3, 5, 7 and 9 were not treated in proficiency evaluation the biases of these runes are presented in Figure 11.

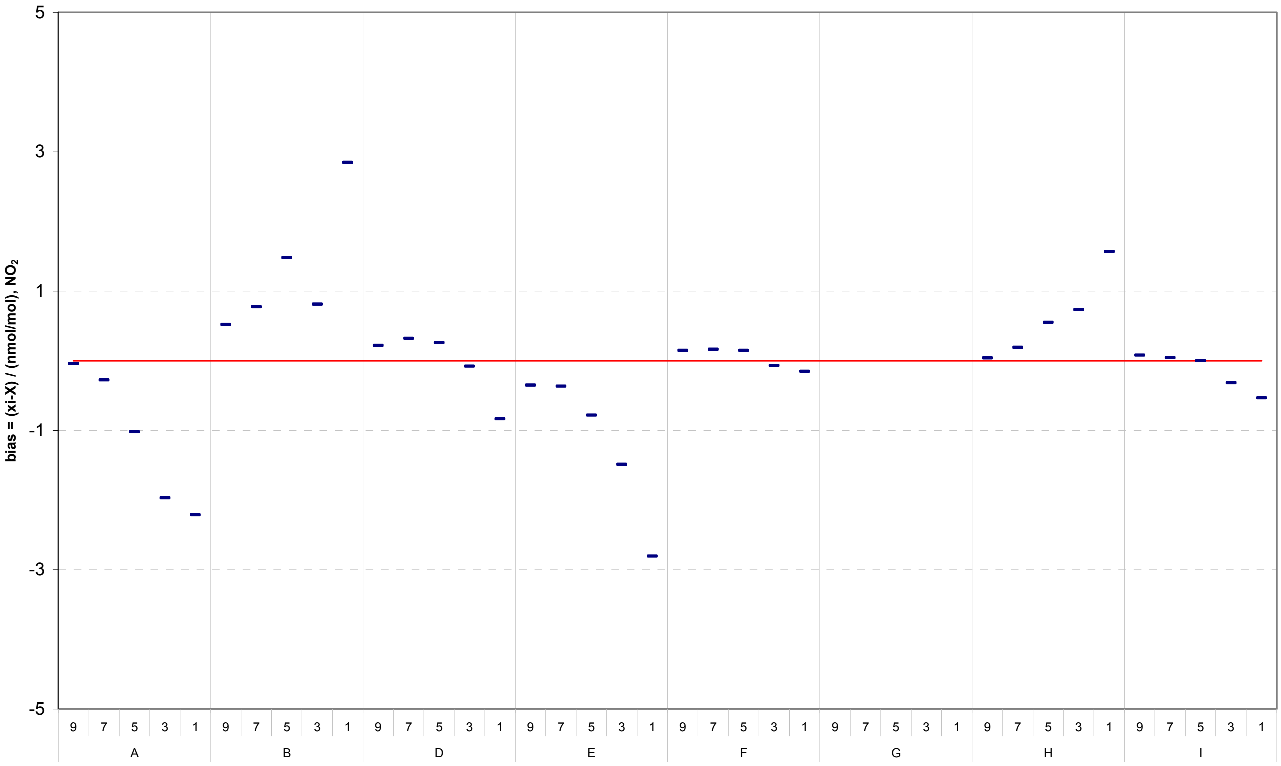

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
At these test gas mixtures the concentration levels of NO_2 were zero and the concentration levels of NO were not zero (see Table 3). In that perspective the figure shows the effect of NO concentration on NO_2 measurements. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

The efficiency of NO_2-to-NO converters of NO_X analyzers

Since NO and NO_2 test gases were produced by gas phase titration it is possible to evaluate the efficiency of NO_2-to-NO converter of each participant's NO_X analyser. The evaluation takes each participants NO and NO_2 measurements before and after oxidation by O_3. The converter efficiency (α) is calculated using equation 3 [4]:

$$\alpha = \frac{[NO2]_i - [NO2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \qquad (3)$$

The O_3 measurements of each participant can also be compared to either NO or NO_2 change by calculating Δ^{NO} or Δ^{NO2} using equation 4 and 5 respectively:

$$\Delta^{NO} = [O3]_{i+1} - ([NO]_{i-1} - [NO]_i) \qquad (4)$$

$$\Delta^{NO2} = [O3]_{i+1} - ([NO2]_i - [NO2]_{i-1}) \qquad (5)$$

Ideal value for α is 100% while for Δ^{NO} and Δ^{NO2} it is 0 nmol/mol.

The evaluation of equation 4 and 5 can not be made at the lowest NO2 level (14 ppb) because, due to insufficient excess of NO, O3 is not completely reduced. The evaluation of equations 3, 4 and 5 for each participant at different concentration levels are given in Table 5.

IE	NO_2	α	Δ^{NO}	Δ^{NO2}
code	nmol/mol	%	nmol/mol	nmol/mol
A	14	100.8		
A	22	100.4	1.1	1.0
A	60	100.7	2.5	2.1
A	100	100.4	2.7	2.3
A	120	99.9	1.9	2.0
B	14	99.7		
B	22	98.2	0.6	1.0
B	60	100.2	3.6	3.5
B	100	99.5	6.6	7.0
B	120	100.8	8.5	7.6
C	14	99.7		
C	22	100.5	0.1	0.0
C	60	100.3	-0.5	-0.6
C	100	100.1	-1.2	-1.2
C	120	99.9	-1.8	-1.6
D	14	100.4		
D	22	99.6	0.4	0.5
D	60	100.2	1.2	1.1
D	100	100.4	1.7	1.3
D	120	100.7	2.1	1.3
E	14	98.9		
E	22	98.7	2.0	2.3
E	60	99.1	4.7	5.2
E	100	99.4	7.7	8.3
E	120	99.7	9.8	10.2

IE	NO_2	α	Δ^{NO}	Δ^{NO2}
code	nmol/mol	%	nmol/mol	nmol/mol
F	14	101.6		
F	22	101.4	-0.2	-0.5
F	60	100.5	-1.2	-1.5
F	100	100.8	-1.6	-2.5
F	120	101.3	-1.3	-2.9
G	14	100.5		
G	22	96.7	1.7	2.4
G	60	97.8	0.5	1.9
G	100	96.7	-2.1	1.4
G	120	98.2	2.2	4.4
H	14	101.8		
H	22	102	-0.2	-0.6
H	60	101.9	-0.6	-1.7
H	100	102.5	-0.3	-2.9
H	120	102.8	0.9	-2.3
I	14	99.8		
I	22	99.8	1.7	1.7
I	60	99.1	3.5	4.0
I	100	98.3	4.1	5.8
I	120	96.7	3.3	7.1

Table 5: The efficiency of NO_2-to-NO converters.

The uncertainty in the evaluation of the converter efficiency decreases as NO_2 concentrations increase. The average standard uncertainty of the converter efficiency was calculated by estimating the standard deviation of repeated measurements of quantities in equation 3 at different NO_2 levels. It was found to be approximately 1%, at 120 nmol/mol of NO_2, and 2%, at 14 nmol/mol of NO_2.

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) that categorises results in seven categories (a1 to a7). The general comments for each category are:

- a1: measurement result is completely satisfactory
- a2: measurement result is satisfactory (z'-score satisfactory and En-number ok) but the reported uncertainty is too high
- a3: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)
- a4: measurement result is questionable (z'-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)
- a5: measurement result is questionable (z'-score questionable and En-number not ok)
- a6: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)
- a7: measurement result is unsatisfactory (z'-score unsatisfactory and En-number not ok)

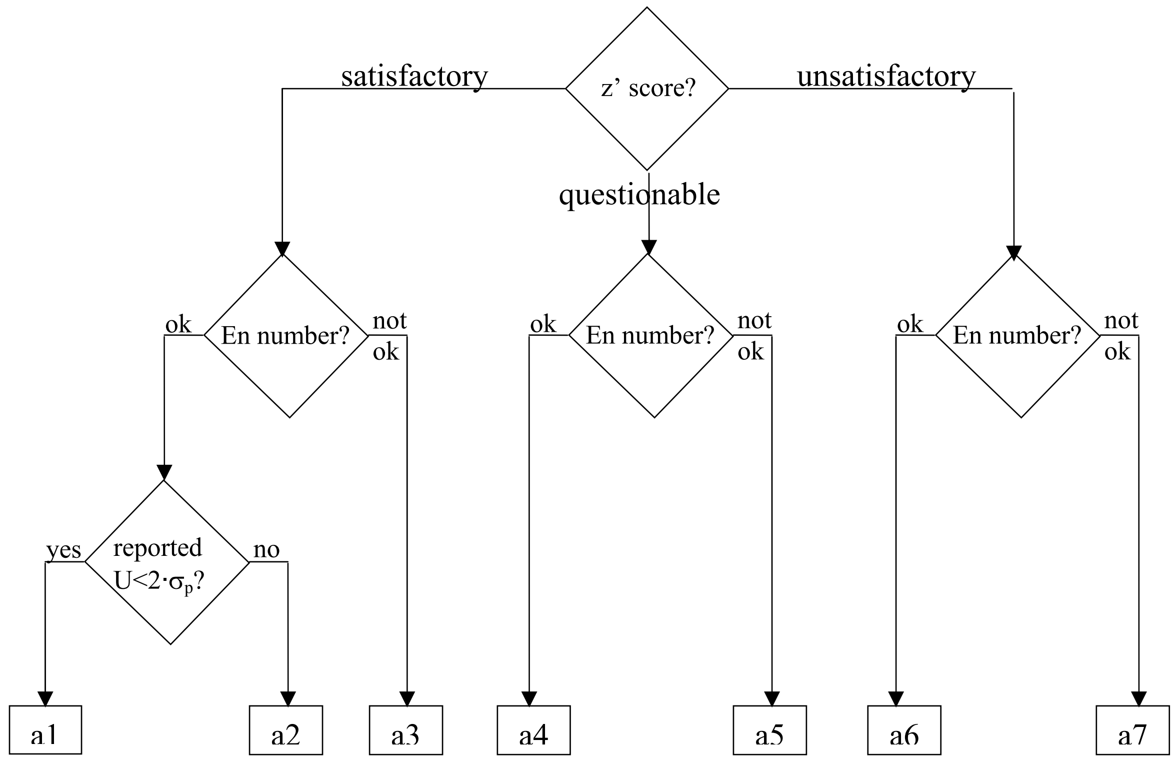

Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in Table 6.

	run number	conc. level	IE code							
			A	B	D	E	F	G	H	I
SO_2 (nmol/mol)	0	0.1	a1	a1	a1	a1	a1	a1	a1	a1
	5	3.0	a1	a1	a1	a1	a1	a1	a3	a1
	4	7.4	a1	a1	a1	a1	a1	a3	a3	a1
	3	18.8	a3	a1	a1	a1	a1	a3	a3	a1
	2	47.9	a3	a1	a1	a1	a1	a1	a3	a1
	1	134.9	a5	a1	a1	a1	a1	a1	a3	a1
CO (µmol/mol)	0	0.014	a1	a1	a1	a1	a1	a1	a3	a1
	5	1.003	a1	a1	a1	a1	a1	a1	a1	a3
	4	1.976	a3	a1	a1	a1	a1	a1	a1	a3
	3	4.272	a1	a1	a1	a3	a1	a1	a1	a1
	2	5.959	a1	a1	a1	a3	a1	a1	a1	a1
	1	8.547	a1	a1	a1	a3	a1	a1	a1	a1
O_3 (nmol/mol)	0	0.4	a1	a2	a1	a1	a1	a1	a1	a1
	5	13.9	a1	a2	a1	a1	a1	a1	a1	a1
	4	20.8	a1	a2	a1	a1	a1	a1	a1	a1
	3	59.2	a1	a1	a1	a5	a1	a1	a1	a1
	2	98.7	a1	a1	a1	a5	a1	a2	a1	a1
	1	117.0	a1	a1	a1	a5	a1	a2	a1	a1
NO (nmol/mol)	0	0.3	a1	a2	a1	a1	a1	a1	a1	a1
	10	3.4	a1	a2	a1	a1	a1	a3	a1	a1
	9	17.1	a1	a1	a1	a1	a1	a1	a1	a1
	8	31.8	a1	a1	a1	a1	a1	a3	a1	a1
	7	52.5	a1	a1	a1	a1	a1	a1	a1	a1
	6	94.9	a1	a1	a1	a1	a1	a1	a1	a1
	5	154.5	a1	a1	a1	a1	a1	a1	a1	a1
	4	154.0	a1	a1	a1	a1	a1	a1	a1	a1
	3	253.8	a1	a1	a1	a1	a1	a2	a1	a1
	2	383.2	a1	a1	a1	a1	a1	a2	a1	a1
	1	502.0	a1	a1	a1	a1	a1	a2	a1	a1
NO_2 (nmol/mol)	0	-0.2	a1	a2	a1	a2	a1	a3	a1	a1
	10	13.5	a1	a2	a1	a1	a1	a1	a1	a1
	8	20.6	a1	a2	a1	a1	a1	a1	a1	a1
	6	59.9	a3	a2	a1	a1	a1	a1	a1	a1
	4	101.3	a1	a4	a1	a1	a1	a1	a1	a1
	2	121.9	a1	a2	a1	a1	a1	a1	a1	a3

Table 6: The general assessment of proficiency results.

8. Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties. In terms of the criteria imposed by the European Commission (σ_p) 85% of the results reported by AQUILA laboratories fall into ‘a1’ category and are good both in terms of measured values and evaluated uncertainties. Among the residual results the majority presented good measured values but the evaluated uncertainties were either too high, category ‘a2’ (6%), or too small, category ‘a3’ (8%). The common IE criterion (standard deviation for proficiency assessment) derives from the European standards’ uncertainty requirements and is confirmed to be realistic by comparison to reproducibility standard deviation obtained at this (Annex C) and previous IEs [20], [21], [22], [23]. However, the European standards’ uncertainty requirements are explicit only at high concentrations while no uncertainty requirements are stated at zero level. For that reason IE criteria at zero concentration were set in AQUILA’s position paper [12]. In the present IE it can be observed an increase in the proportion of ‘a1’ results and a decrease of ‘a2’ results with respect to previous IEs. The last could be considered as an improvement in the ability of NRLs to estimate their uncertainty (not too high, not too small) but may also reflect the effect of the new (more tolerant) criteria for uncertainty at zero level implemented in 2009 for the first time.
Laboratory E presented overall unsatisfactory results of the z’-score evaluation for O_3 (two or more questionable results), therefore participation to the next IE is required in order to demonstrate remediation measures. In addition, laboratories A and B presented one questionable result each, for SO_2 and NO_2 respectively. According to the protocol in force these performances are considered as a warning and no action is required.

The best comparability of results among AQUILA participants is the one observed in NO measurements while NO_2 and SO_2 measurement methods were those with the poorer performance. The relative reproducibility limits, at the highest studied concentration levels, are 7.9% for CO, 8.9% for O_3 and 2.0% for NO, all below the objective derived from criteria imposed by the European Commission (σ_p). This is not the case for NO_2 and SO_2 where the relative reproducibility limits are 10.9% and 11.4% respectively while the objectives are 9.5% and 10.2%. The reproducibility of these two measurement methods in this IE is therefore generally considered as unsatisfactory. An inadequate comparability among participants SO_2 measurements had been already reported in previous IEs suggesting that further investigation to identify the causes is needed.

9. References

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Annex A. Assigned values

The assigned values of tested concentration levels (run) were derived from ERLAPs measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [13].

ERLAP's SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [6]. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [8]. All flows were measured with a certified volumeter. For O_3 measurements, the analyzers were calibrated using the JRC SRP42 primary standard (constructed by NIST) which has been compared to BIPM primary standard [24]. The photometer absorption cross section uncertainty (1.06%) was included in the uncertainty budget [25] [26].

The reference gas mixture composition evaluation and the calibration experiment evaluation were carried out using two computer applications, the "GUM WORKBENCH" [27] and "B-least" [28] respectively. For extending calibration from the NO to NO_2 channel of NO_X analyser the GPT test was performed to establish the efficiency of NO_2-converter.

ERLAP's measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [13]. The validation is taking into account ERLAP's measurement result (X) and its standard uncertainty ($u_{X'}$) as given in expression 6 [13]:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_{X'}^2}} < 2 \qquad (6)$$

Where 'x*' and 's*' represent robust average and robust standard deviation respectively and 'p' is the number of participants.

In
Table 7 all inputs for expression 6 are given and all ERLAP's measurement results are confirmed to be valid.

run	unit	X	uX'	x*	s*	p	val.
NO _0	nmol/mol	0.30	0.32	0.23	0.58	9	OK
NO _1	nmol/mol	501.98	7.18	502.84	2.78	9	OK
NO _2	nmol/mol	383.20	5.49	384.62	3.48	9	OK
NO _3	nmol/mol	253.84	3.66	253.75	2.00	9	OK
NO _4	nmol/mol	153.96	2.26	154.20	2.79	9	OK
NO _5	nmol/mol	154.50	2.27	153.73	1.70	9	OK
NO _6	nmol/mol	94.86	1.43	94.80	1.91	9	OK
NO _7	nmol/mol	52.49	0.85	51.83	1.61	9	OK
NO _8	nmol/mol	31.80	0.59	31.72	0.91	9	OK
NO _9	nmol/mol	17.07	0.43	16.71	0.80	9	OK
NO _10	nmol/mol	3.37	0.33	3.36	0.50	9	OK
NO2 _0	nmol/mol	-0.22	0.12	0.02	0.27	9	OK
NO2 _1	nmol/mol	3.24	1.09	2.63	2.23	8	OK
NO2 _2	nmol/mol	121.89	1.67	119.04	3.50	9	OK
NO2 _3	nmol/mol	1.32	0.60	0.92	1.08	8	OK
NO2 _4	nmol/mol	101.27	1.29	99.86	3.87	9	OK
NO2 _5	nmol/mol	0.11	0.46	0.18	0.35	8	OK
NO2 _6	nmol/mol	59.90	0.81	58.94	2.18	9	OK
NO2 _7	nmol/mol	-0.14	0.26	-0.04	0.19	8	OK
NO2 _8	nmol/mol	20.65	0.36	20.22	0.87	9	OK
NO2 _9	nmol/mol	-0.14	0.20	-0.06	0.15	8	OK
NO2 _10	nmol/mol	13.52	0.23	13.41	0.74	9	OK

run	unit	X	uX'	x*	s*	p	val.
CO _0	µmol/mol	0.01	0.01	0.00	0.02	9	OK
CO _1	µmol/mol	8.55	0.05	8.48	0.17	9	OK
CO _2	µmol/mol	5.96	0.05	5.95	0.14	9	OK
CO _3	µmol/mol	4.27	0.05	4.28	0.13	9	OK
CO _4	µmol/mol	1.98	0.02	1.98	0.07	9	OK
CO _5	µmol/mol	1.00	0.03	1.00	0.05	9	OK
O3 _0	nmol/mol	0.36	0.38	0.01	0.29	9	OK
O3 _1	nmol/mol	117.03	0.96	119.01	2.40	9	OK
O3 _2	nmol/mol	98.70	0.83	100.42	2.01	9	OK
O3 _3	nmol/mol	59.16	0.56	60.01	1.17	9	OK
O3 _4	nmol/mol	20.75	0.44	20.90	0.72	9	OK
O3 _5	nmol/mol	13.94	0.48	13.94	0.48	9	OK
SO2 _0	nmol/mol	0.08	0.22	0.01	0.18	9	OK
SO2 _1	nmol/mol	134.88	0.90	134.30	2.86	9	OK
SO2 _2	nmol/mol	47.93	0.39	47.99	1.63	9	OK
SO2 _3	nmol/mol	18.84	0.26	18.98	1.04	9	OK
SO2 _4	nmol/mol	7.40	0.23	7.44	0.56	9	OK
SO2 _5	nmol/mol	3.00	0.23	3.00	0.31	9	OK

Table 7: The validation of assigned values (X)
by comparison to the robust averages (x*) with taking into the account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by expression 6.

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. From the relative differences between beginning and end measurements, average and standard deviation were calculated, and the uncertainty of test gas due to lack of homogeneity was calculated as the sum of squares of these average and standard deviation. The upper and lower limits of bias due to homogeneity was evaluated to be smaller than 0.5% which constitutes the relative standard uncertainty of 0,3% of each concentration level. The standard uncertainties of assigned/reference values (u_X) were calculated with equation 7 and used in the proficiency evaluations of chapter 5.

$$u_X^2 = u_{X'}^2 + \left(X \cdot u_{homogeneity}\right)^2 \qquad (7)$$

Annex B. The results of the IE

In this annex are reported participant's results, presented both in tables and graphs. For each run, participants were asked to report 3 results representing 30 minutes measurement each (x_{ij}). In this annex are presented the reported data and their uncertainty $u(x_i)$ and $U(x_i)$) expressed in mol/mol units. For all the runs except concentration levels 0, also average (x_i) and standard deviation (s_i) of each participant are presented. As a group evaluation robust average (x*) and robust standard deviation (s*) were calculated (applying the procedure described in Annex C of ISO 13528) for each run, and are presented in the following tables. The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ($U(x_i)$) are indicated with error bars.

Reported values for SO_2

parameter: SO_2				all units are nmol/mol					
run: 0				x*: 0.0		s*: 0.2			
	A	B	C	D	E	F	G	H	I
xi,1	0.50	-0.44	0.08	-0.03	0.19	0.10	0.00	0.00	-0.30
u(xi)	0.54	0.46	0.22	0.20	0.50	0.54	0.00	0.00	1.00
U(xi)	1.08	0.92	0.44	0.40	1.00	1.08	0.00	0.00	1.96

Table 8: Reported values for SO_2 run 0.

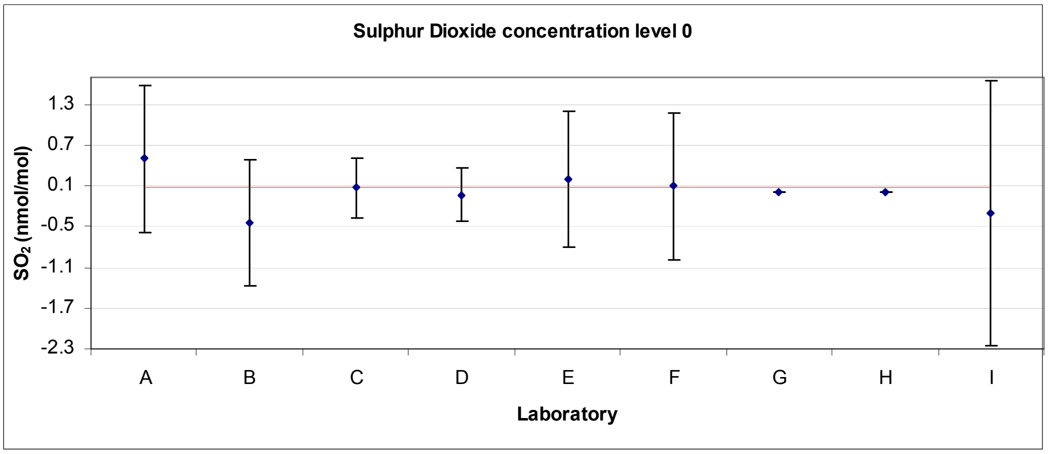

Figure 13: Reported values for SO_2 run 0.

parameter: SO_2					all units are nmol/mol				
run: 1					x*: 134.3		s*: 2.9		
	A	B	C	D	E	F	G	H	I
xi,1	144.39	133.76	134.80	132.18	132.62	139.58	133.00	130.49	138.96
xi,2	143.28	133.73	134.89	131.97	132.69	139.38	132.80	130.66	138.82
xi,3	143.66	133.67	134.96	132.18	132.55	139.62	132.80	130.67	138.88
xi	143.78	133.72	134.88	132.11	132.62	139.53	132.87	130.61	138.89
si	0.56	0.05	0.08	0.12	0.07	0.13	0.12	0.10	0.07
u(xi)	2.51	3.63	0.80	2.15	1.70	2.29	1.85	1.11	3.32
U(xi)	5.03	7.27	1.60	4.30	3.39	4.58	3.70	2.22	6.51

Table 9: Reported values for SO_2 run 1.

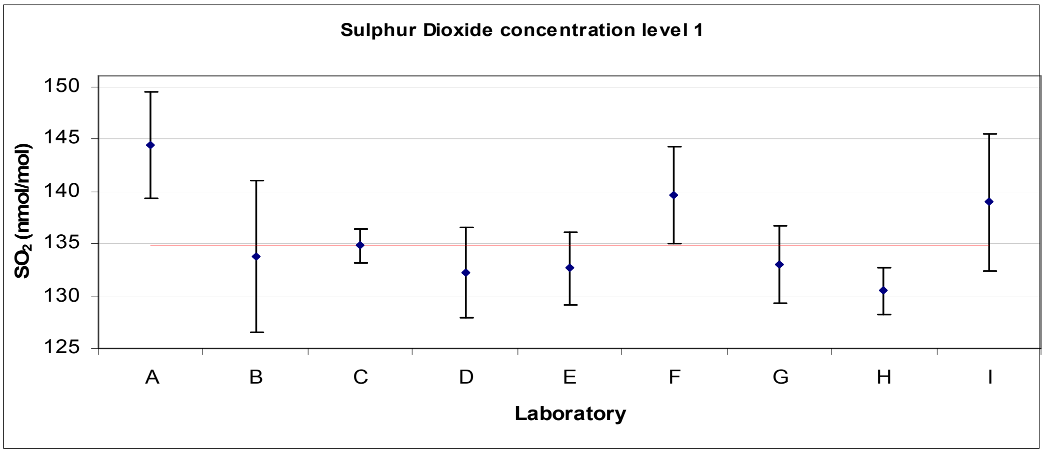

Figure 14: Reported values for SO_2 run 1.

parameter: SO_2					all units are nmol/mol				
run: 2					x*: 48.0		s*: 1.6		
	A	B	C	D	E	F	G	H	I
xi,1	51.29	47.20	47.92	46.99	47.08	49.77	48.20	45.39	49.34
xi,2	51.24	47.09	47.91	46.96	47.01	49.45	47.90	45.28	49.45
xi,3	51.12	47.05	47.97	46.94	47.01	49.61	48.00	45.16	49.27
xi	51.22	47.11	47.93	46.96	47.03	49.61	48.03	45.28	49.35
si	0.09	0.08	0.03	0.03	0.04	0.16	0.15	0.12	0.09
u(xi)	0.89	1.38	0.36	0.90	0.93	0.96	0.75	0.39	1.51
U(xi)	1.79	2.76	0.72	1.80	1.85	1.91	1.50	0.78	2.95

Table 10: Reported values for SO_2 run 2.

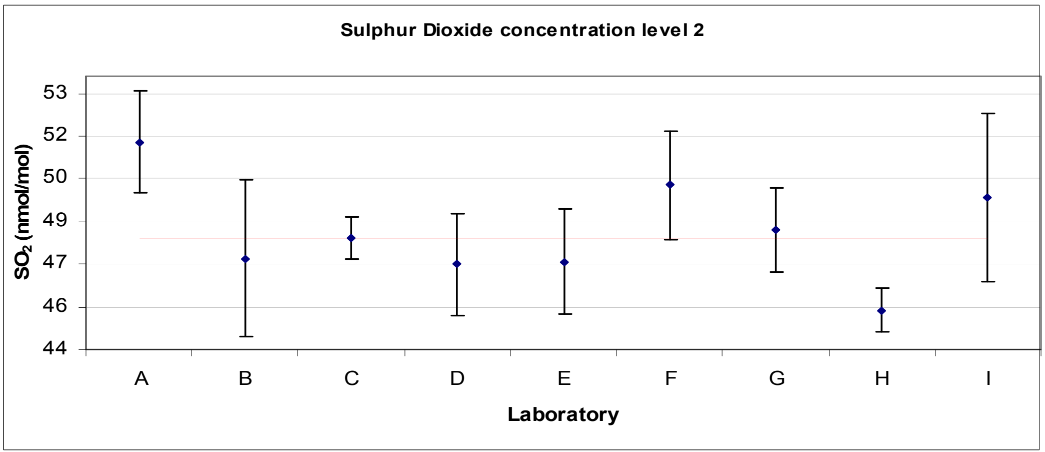

Figure 15: Reported values for SO_2 run 2.

parameter: SO_2					all units are nmol/mol				
run: 3					x*: 19.0		s*: 1.0		
	A	B	C	D	E	F	G	H	I
xi,1	20.38	18.25	18.87	18.42	18.39	19.76	20.80	16.63	19.43
xi,2	20.12	18.19	18.85	18.39	18.41	19.59	20.80	16.63	19.33
xi,3	19.88	18.32	18.81	18.38	18.41	19.69	20.80	16.67	19.46
xi	20.13	18.25	18.84	18.40	18.40	19.68	20.80	16.64	19.41
si	0.25	0.07	0.03	0.02	0.01	0.09	0.00	0.02	0.07
u(xi)	0.54	0.72	0.25	0.60	0.67	0.63	0.30	0.14	1.09
U(xi)	1.08	1.44	0.50	1.20	1.34	1.25	0.60	0.28	2.14

Table 11: Reported values for SO_2 run 3.

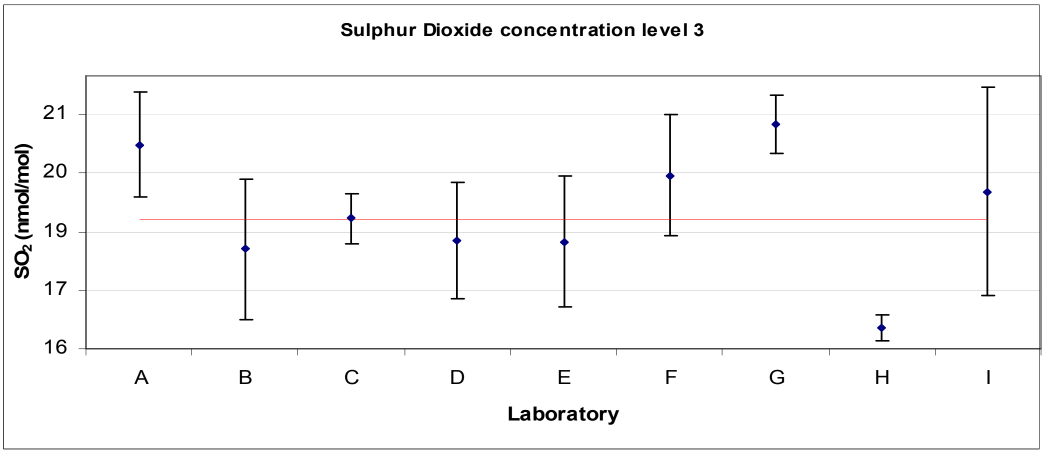

Figure 16: Reported values for SO_2 run 3.

parameter: SO_2					all units are nmol/mol				
run: 4					x*: 7.4		s*: 0.6		
	A	B	C	D	E	F	G	H	I
xi,1	8.78	6.92	7.39	7.18	7.17	7.70	8.50	5.62	7.67
xi,2	8.00	6.97	7.41	7.16	7.22	7.72	8.40	5.51	7.68
xi,3	8.05	6.89	7.40	7.20	7.22	7.72	8.50	5.50	7.69
xi	8.28	6.93	7.40	7.18	7.20	7.71	8.47	5.54	7.68
si	0.44	0.04	0.01	0.02	0.03	0.01	0.06	0.07	0.01
u(xi)	0.54	0.52	0.23	0.45	0.57	0.56	0.14	0.06	1.02
U(xi)	1.08	1.04	0.46	0.90	1.13	1.11	0.28	0.12	1.99

Table 12: Reported values for SO_2 run 4.

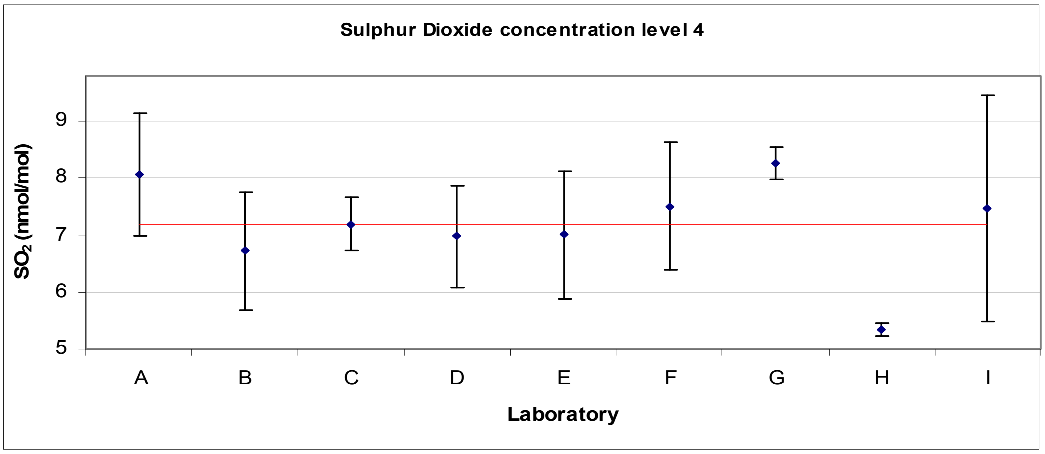

Figure 17: Reported values for SO_2 run 4.

parameter: SO_2				all units are nmol/mol					
	run: 5			x*: 3.0		s*: 0.3			
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	3.51	2.57	3.01	2.86	2.95	3.19	3.30	1.12	3.18
xi,2	3.21	2.54	2.99	2.87	2.86	3.18	3.30	1.09	3.12
xi,3	3.46	2.59	3.00	2.87	2.82	3.14	3.30	1.11	3.13
xi	3.39	2.57	3.00	2.87	2.88	3.17	3.30	1.11	3.14
si	0.16	0.03	0.01	0.01	0.07	0.03	0.00	0.02	0.03
u(xi)	0.54	0.48	0.23	0.25	0.53	0.54	0.08	0.01	1.00
U(xi)	1.08	0.96	0.46	0.50	1.06	1.09	0.16	0.02	1.97

Table 13: Reported values for SO_2 run 5.

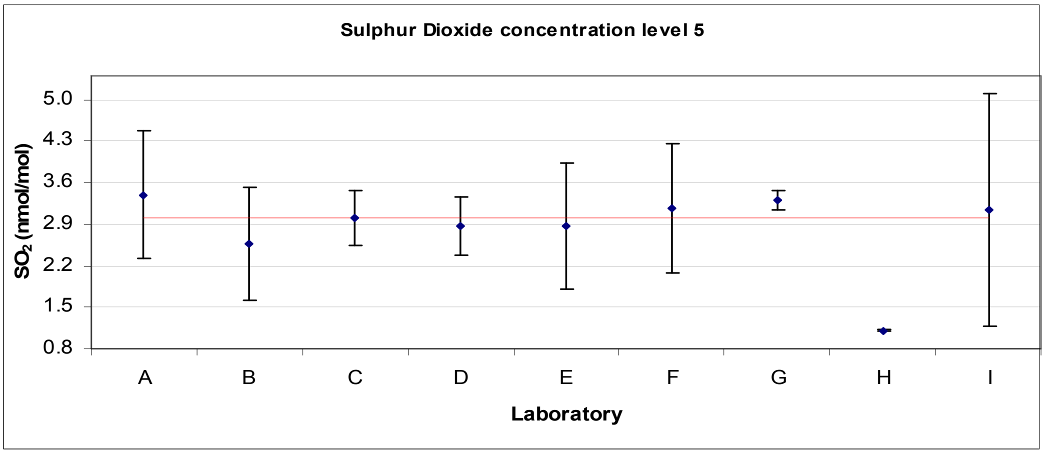

Figure 18: Reported values for SO_2 run 5.

Reported values for CO

parameter:	CO			all units are µmol/mol					
run:	0			x*:	0.00	s*:	0.02		
	A	B	C	D	E	F	G	H	I
xi,1	0.000	-0.049	0.014	0.000	0.003	0.019	0.010	-0.039	0.030
u(xi)	0.071	0.049	0.010	0.020	0.030	0.080	0.000	-0.002	0.050
U(xi)	0.142	0.097	0.020	0.040	0.060	0.170	0.000	-0.002	0.100

Table 14: Reported values for CO run 0.

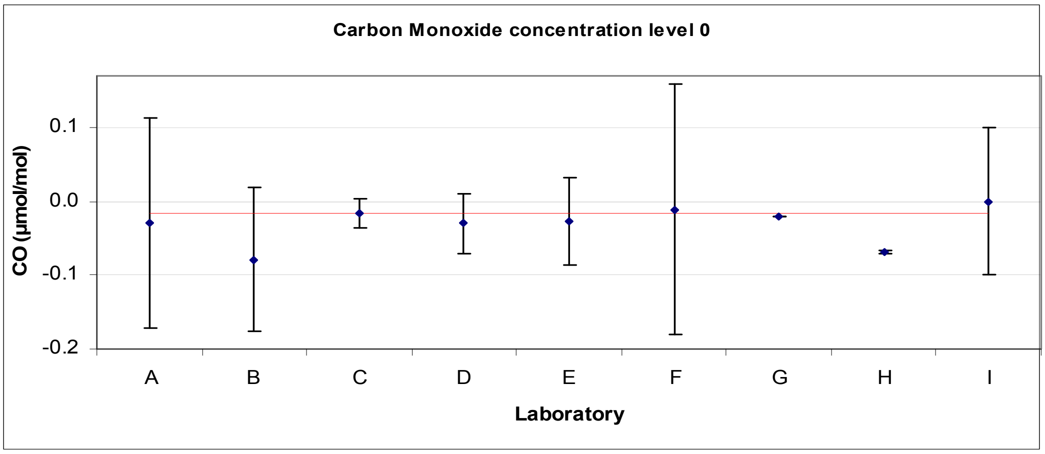

Figure 19: Reported values for CO run 0.

parameter:	CO			all units are µmol/mol					
run:	1			x*:	8.48	s*:	0.17		
	A	B	C	D	E	F	G	H	I
xi,1	8.493	8.663	8.545	8.388	8.129	8.397	8.760	8.289	8.510
xi,2	8.493	8.665	8.538	8.394	8.123	8.417	8.750	8.298	8.490
xi,3	8.506	8.669	8.559	8.393	8.120	8.417	8.760	8.305	8.480
xi	8.497	8.666	8.547	8.392	8.124	8.410	8.757	8.297	8.493
si	0.008	0.003	0.011	0.003	0.005	0.012	0.006	0.008	0.015
u(xi)	0.071	0.136	0.040	0.140	0.108	0.250	0.120	0.256	0.200
U(xi)	0.142	0.272	0.080	0.280	0.216	0.500	0.240	0.512	0.390

Table 15: Reported values for CO run 1.

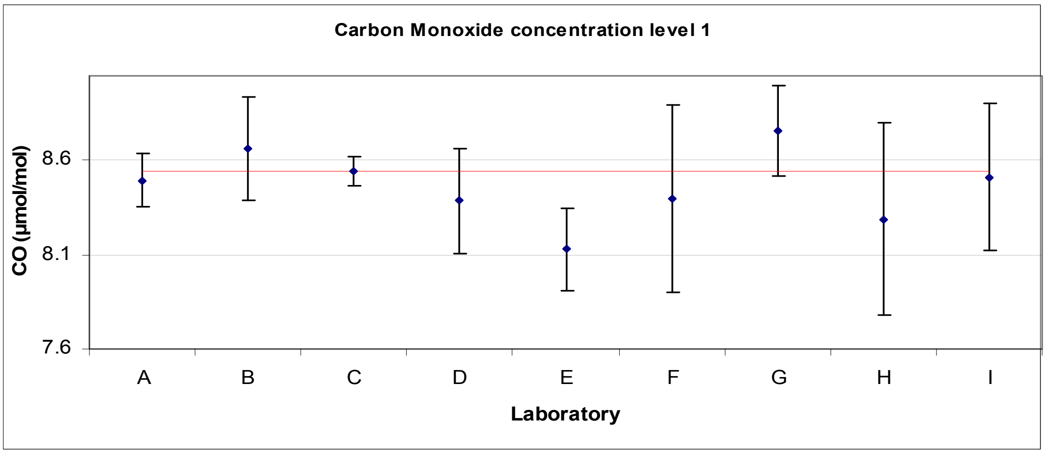

Figure 20: Reported values for CO run 1.

parameter:	CO			all units are µmol/mol					
run:	2			x*:	5.95	s*:	0.14		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	6.049	6.043	5.963	5.863	5.680	5.881	6.110	5.829	6.040
xi,2	6.049	6.042	5.955	5.860	5.677	5.889	6.110	5.840	6.040
xi,3	6.052	6.041	5.960	5.866	5.672	5.889	6.110	5.840	6.030
xi	6.050	6.042	5.959	5.863	5.676	5.886	6.110	5.836	6.037
si	0.002	0.001	0.004	0.003	0.004	0.005	0.000	0.006	0.006
u(xi)	0.071	0.101	0.048	0.110	0.085	0.190	0.080	0.180	0.150
U(xi)	0.142	0.202	0.095	0.210	0.169	0.370	0.160	0.360	0.290

Table 16: Reported values for CO run 2.

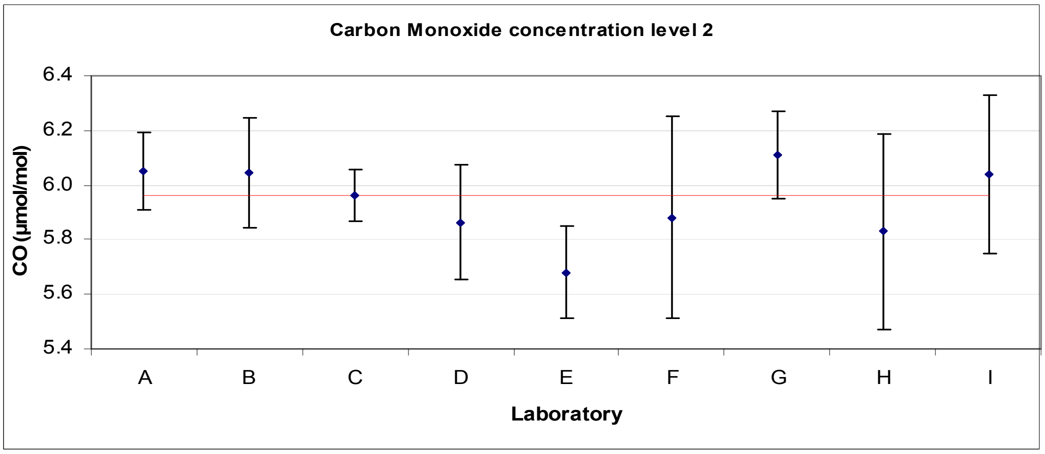

Figure 21: Reported values for CO run 2.

parameter:	CO			all units are µmol/mol					
run:	3			x*:	4.28	s*:	0.13		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	4.399	4.323	4.274	4.210	4.076	4.257	4.390	4.186	4.420
xi,2	4.399	4.321	4.279	4.211	4.077	4.258	4.390	4.172	4.420
xi,3	4.422	4.320	4.262	4.211	4.072	4.262	4.380	4.184	4.430
xi	4.407	4.321	4.272	4.211	4.075	4.259	4.387	4.181	4.423
si	0.013	0.002	0.009	0.001	0.003	0.003	0.006	0.008	0.006
u(xi)	0.071	0.080	0.045	0.085	0.070	0.140	0.060	0.129	0.110
U(xi)	0.142	0.160	0.090	0.170	0.139	0.290	0.120	0.258	0.220

Table 17: Reported values for CO run 3.

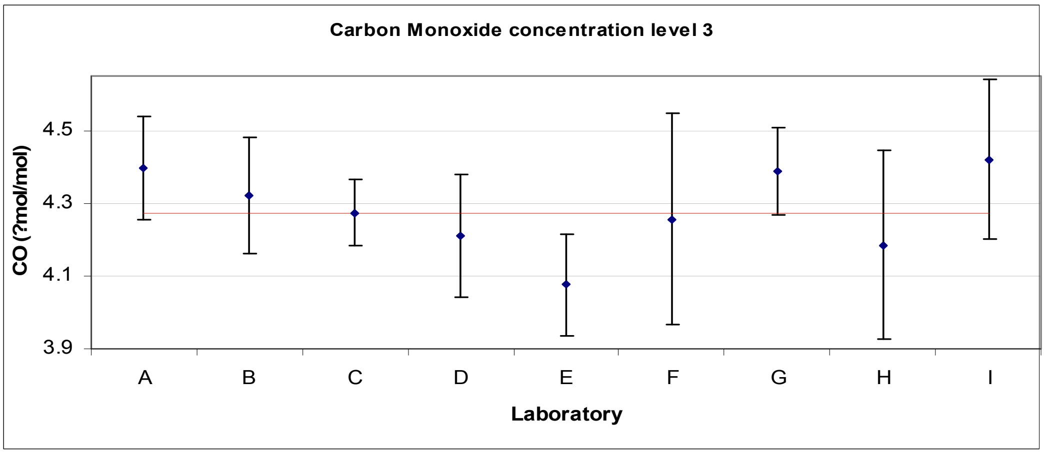

Figure 22: Reported values for CO run 3.

parameter:	CO			all units are µmol/mol					
run:	4			x*:	1.98		s*:	0.07	
	A	B	C	D	E	F	G	H	I
xi,1	2.148	1.966	1.972	1.939	1.881	1.987	2.020	1.927	2.190
xi,2	2.148	1.967	1.969	1.939	1.880	1.981	2.020	1.938	2.180
xi,3	2.148	1.966	1.987	1.939	1.880	1.984	2.020	1.944	2.190
xi	2.148	1.966	1.976	1.939	1.880	1.984	2.020	1.936	2.187
si	0.000	0.001	0.010	0.000	0.001	0.003	0.000	0.009	0.006
u(xi)	0.071	0.056	0.023	0.055	0.049	0.100	0.030	0.060	0.070
U(xi)	0.142	0.113	0.045	0.110	0.097	0.210	0.060	0.120	0.140

Table 18: Reported values for CO run 4.

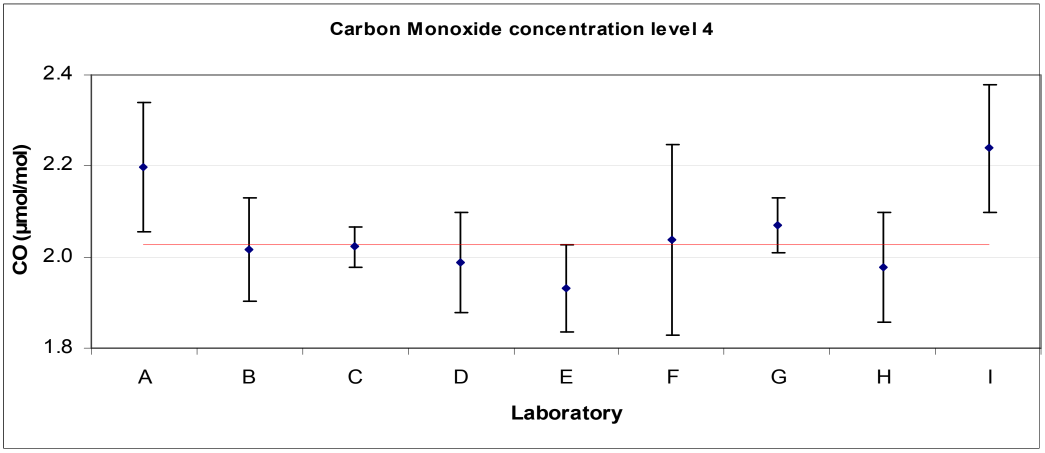

Figure 23: Reported values for CO run 4.

parameter:	CO			all units are µmol/mol					
run:	5			x*:	1.00		s*:	0.05	
	A	B	C	D	E	F	G	H	I
xi,1	1.074	0.962	1.004	0.974	0.952	1.005	1.020	0.971	1.140
xi,2	1.074	0.959	0.994	0.973	0.950	1.012	1.020	0.974	1.150
xi,3	1.074	0.960	1.012	0.972	0.950	1.012	1.020	0.975	1.150
xi	1.074	0.960	1.003	0.973	0.951	1.010	1.020	0.973	1.147
si	0.000	0.002	0.009	0.001	0.001	0.004	0.000	0.002	0.006
u(xi)	0.071	0.050	0.031	0.035	0.040	0.090	0.010	0.030	0.060
U(xi)	0.142	0.101	0.062	0.070	0.079	0.180	0.020	0.060	0.110

Table 19: Reported values for CO run 5.

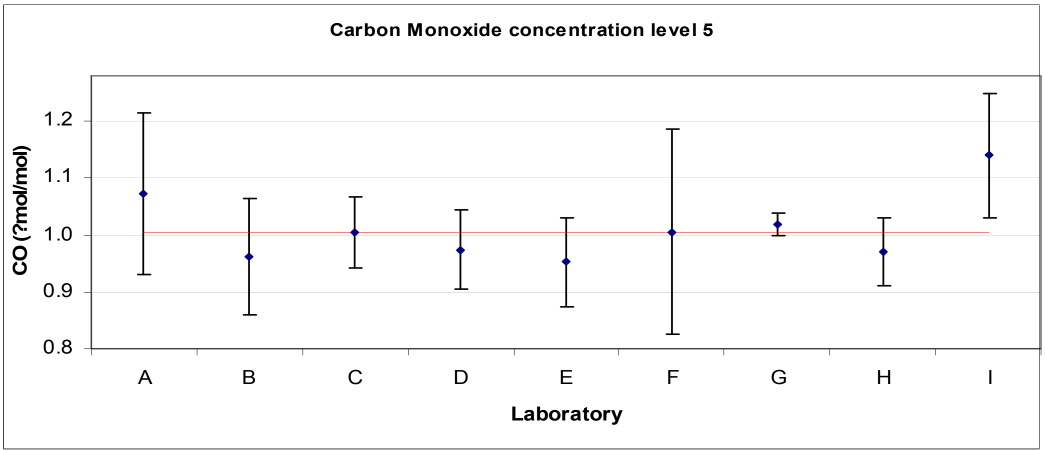

Figure 24: Reported values for CO run 5.

Reported values for O_3

parameter: O_3					all units are nmol/mol				
run: 0					x*: 0.0		s*: 0.3		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	0.10	-0.69	0.36	-0.09	0.42	0.16	0.30	0.00	-0.40
u(xi)	0.930	1.700	0.376	0.450	1.000	0.310	0.010	0.500	0.500
U(xi)	1.86	3.39	0.76	0.90	2.00	0.63	0.02	1.00	0.98

Table 20: Reported values for O_3 run 0.

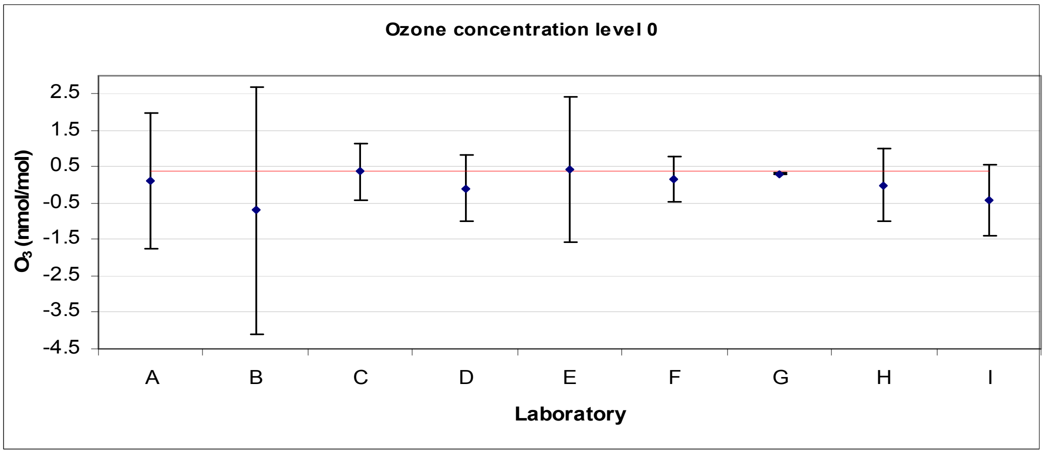

Figure 25: Reported values for O3 run 0.

parameter: O_3					all units are nmol/mol				
run: 1					x*: 119.0		s*: 2.4		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	117.36	116.92	116.55	118.44	126.25	117.09	122.80	118.54	118.56
xi,2	118.62	117.63	117.18	119.26	126.95	117.76	122.50	119.06	119.36
xi,3	119.09	117.90	117.36	119.47	127.12	117.57	122.20	119.31	119.66
xi	118.36	117.48	117.03	119.06	126.77	117.47	122.50	118.97	119.19
si	0.90	0.51	0.43	0.54	0.46	0.35	0.30	0.39	0.57
u(xi)	1.85	3.24	0.89	1.65	2.10	1.14	3.56	1.70	2.44
U(xi)	3.69	6.48	1.79	3.30	4.19	2.85	7.12	3.40	4.77

Table 21: Reported values for O_3 run 1

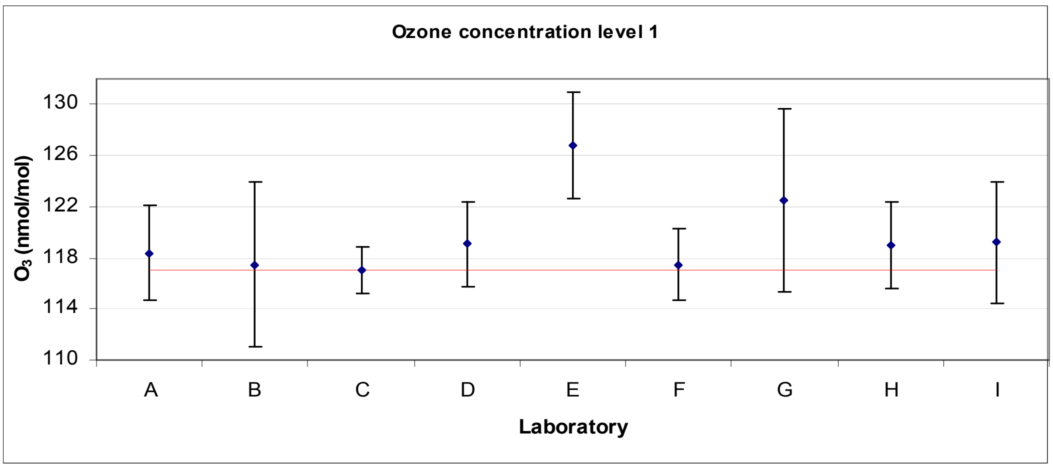

Figure 26: Reported values for O_3 run 1.

parameter: O_3					all units are nmol/mol				
	run: 2				x*: 100.4		s*: 2.0		
	A	B	C	D	E	F	G	H	I
xi,1	99.80	98.69	98.12	99.79	106.21	98.59	103.90	99.80	100.08
xi,2	100.63	99.26	98.87	100.54	107.03	99.31	103.80	100.38	100.70
xi,3	100.89	99.47	99.12	100.78	107.24	99.11	104.10	100.58	101.05
xi	100.44	99.14	98.70	100.37	106.83	99.00	103.93	100.25	100.61
si	0.57	0.40	0.52	0.52	0.54	0.37	0.15	0.41	0.49
u(xi)	1.56	2.87	0.78	1.45	1.92	1.21	3.82	1.52	2.07
U(xi)	3.13	5.75	1.56	2.90	3.84	2.42	7.64	3.04	4.06

Table 22: Reported values for O_3 run 2.

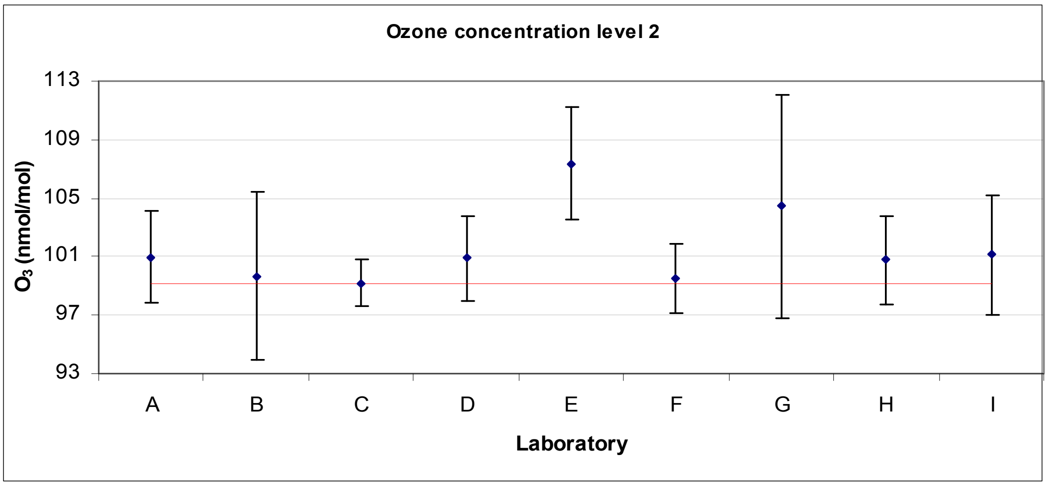

Figure 27: Reported values for O_3 run 2.

parameter: O_3					all units are nmol/mol				
	run: 3				x*: 60.0		s*: 1.2		
	A	B	C	D	E	F	G	H	I
xi,1	60.15	58.92	59.17	60.07	63.92	59.14	61.00	59.99	60.30
xi,2	60.19	59.02	59.18	60.14	64.02	59.28	61.10	59.96	60.36
xi,3	60.18	59.01	59.14	60.17	64.02	59.23	61.10	59.98	60.35
xi	60.17	58.98	59.16	60.13	63.99	59.22	61.07	59.98	60.34
si	0.02	0.06	0.02	0.05	0.06	0.07	0.06	0.02	0.03
u(xi)	0.93	2.18	0.53	1.05	1.56	0.89	1.78	1.10	1.31
U(xi)	1.86	4.36	1.07	2.10	3.11	1.90	3.56	2.20	2.56

Table 23: Reported values for O_3 run 3.

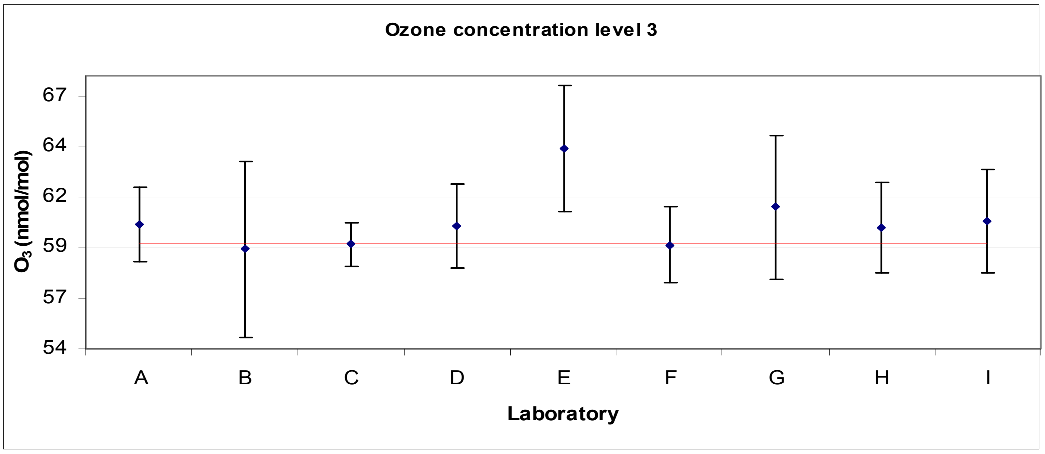

Figure 28: Reported values for O_3 run 3.

parameter: O_3					all units are nmol/mol				
		run: 4			x*: 20.9		s*: 0.7		
	A	B	C	D	E	F	G	H	I
xi,1	20.85	19.88	20.72	20.90	22.50	20.46	22.60	20.84	21.05
xi,2	20.96	19.92	20.81	20.90	22.58	20.50	22.60	20.87	21.01
xi,3	20.92	19.98	20.73	20.91	22.65	20.49	22.70	20.79	21.07
xi	20.91	19.93	20.75	20.90	22.58	20.48	22.63	20.83	21.04
si	0.06	0.05	0.05	0.01	0.08	0.02	0.06	0.04	0.03
u(xi)	0.93	1.76	0.44	0.80	1.20	0.42	0.91	0.71	0.65
U(xi)	1.86	3.51	0.88	1.60	2.39	0.84	1.82	1.42	1.28

Table 24: Reported values for O_3 run 4.

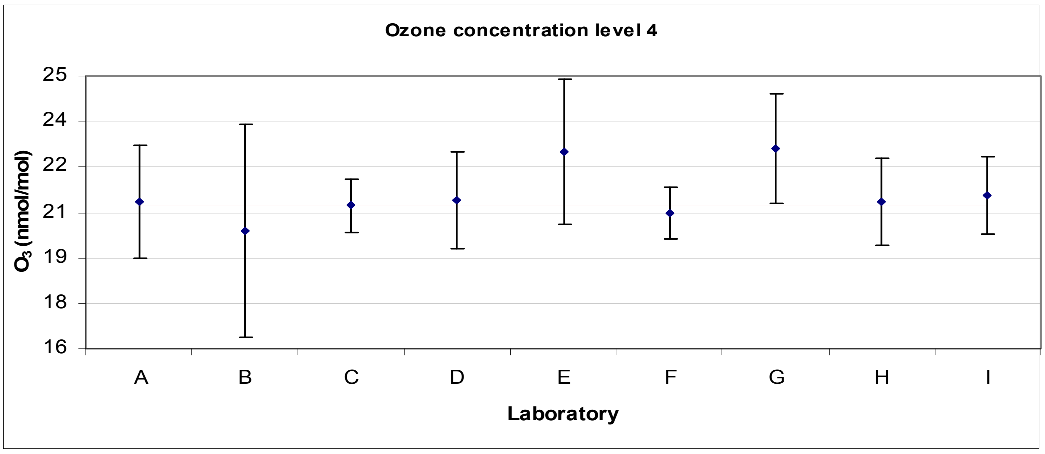

Figure 29: Reported values for O_3 run 4.

parameter: O_3					all units are nmol/mol				
		run: 5			x*: 13.9		s*: 0.5		
	A	B	C	D	E	F	G	H	I
xi,1	13.98	13.04	13.97	13.91	15.26	13.68	14.60	13.95	13.97
xi,2	13.96	13.07	13.90	13.94	15.33	13.66	14.60	13.97	14.05
xi,3	13.90	13.10	13.95	13.98	15.32	13.66	14.40	14.00	14.06
xi	13.95	13.07	13.94	13.94	15.30	13.67	14.53	13.97	14.03
si	0.04	0.03	0.04	0.04	0.04	0.01	0.12	0.03	0.05
u(xi)	0.93	1.72	0.48	0.80	1.14	0.36	0.63	0.64	0.57
U(xi)	1.86	3.44	0.96	1.60	2.27	0.72	1.26	1.28	1.12

Table -25: Reported values for O_3 run 5.

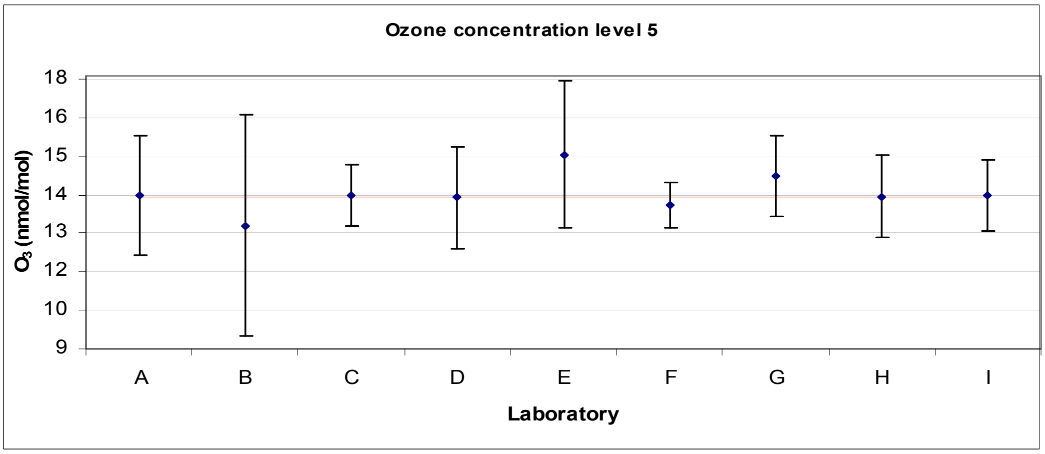

Figure 30: Reported values for O_3 run 5.

Reported values for NO

parameter:	NO				all units are nmol/mol				
run:	0				x*:	0.2	s*:	0.6	
	A	B	C	D	E	F	G	H	I
xi,1	0.80	-1.22	0.30	0.13	1.44	0.11	0.10	0.52	-0.29
u(xi)	0.52	1.35	0.32	0.30	0.68	0.38	0.01	0.01	1.00
U(xi)	1.05	2.70	0.64	0.60	1.36	0.77	0.02	0.02	1.96

Table 26: Reported values for NO run 0.

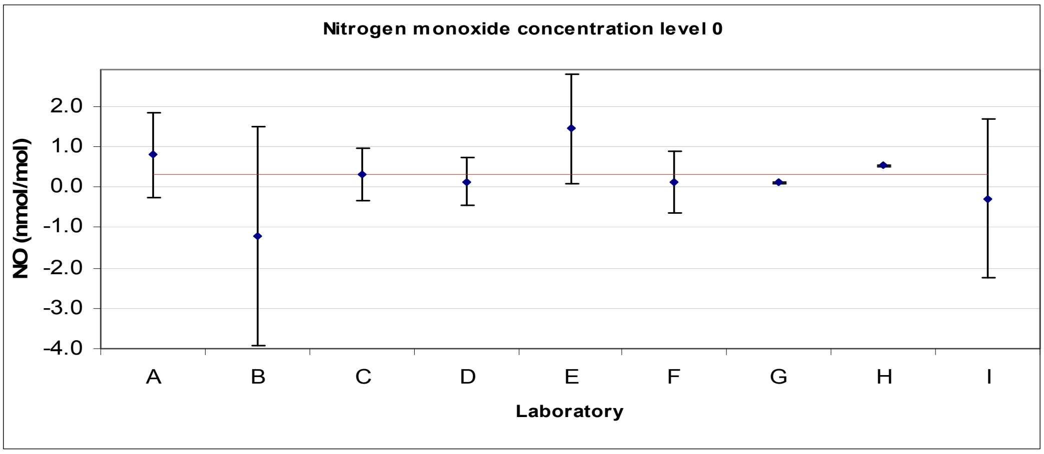

Figure 31: Reported values for NO run 0.

parameter:	NO				all units are nmol/mol				
run:	1				x*:	502.8	s*:	2.8	
	A	B	C	D	E	F	G	H	I
xi,1	503.75	481.97	501.53	497.93	499.66	504.32	504.80	505.76	503.05
xi,2	504.47	482.58	501.96	498.54	500.26	504.85	504.70	506.60	503.49
xi,3	504.60	482.65	502.46	499.15	500.63	504.81	504.90	507.30	503.32
xi	504.27	482.40	501.98	498.54	500.18	504.66	504.80	506.55	503.29
si	0.46	0.37	0.47	0.61	0.49	0.30	0.10	0.77	0.22
u(xi)	5.34	8.05	7.03	6.70	7.34	8.04	14.49	8.12	11.52
U(xi)	10.69	16.10	14.05	13.40	14.67	16.09	28.98	16.24	22.58

Table 27: Reported values for NO run 1.

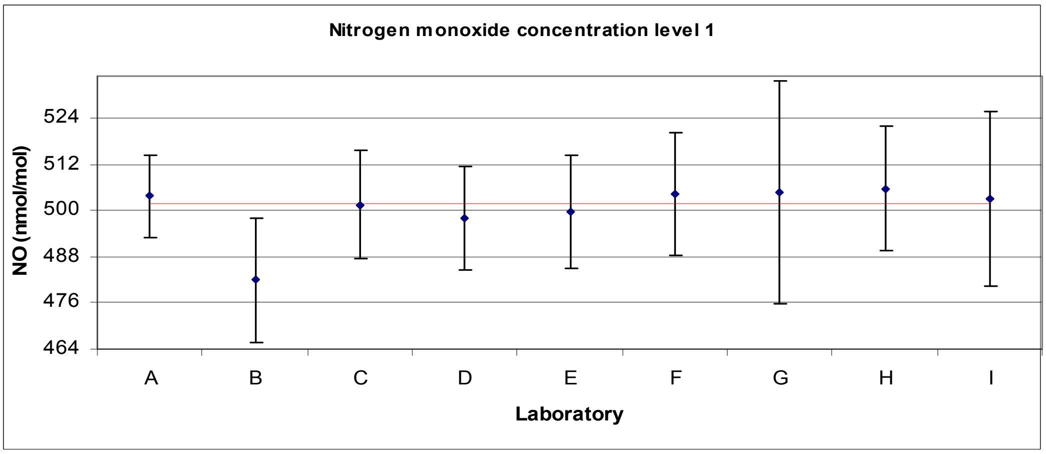

Figure 32: Reported values for NO run 1.

parameter:	NO			all units are nmol/mol					
run:	2			x*: 384.6		s*: 3.5			
	A	B	C	D	E	F	G	H	I
xi,1	387.09	372.87	383.05	381.36	383.08	385.74	384.30	388.20	387.04
xi,2	387.90	373.46	383.20	381.56	383.31	385.99	384.60	388.61	387.81
xi,3	388.55	373.81	383.34	381.77	383.38	385.94	384.70	388.70	387.35
xi	387.85	373.38	383.20	381.56	383.26	385.89	384.53	388.50	387.40
si	0.73	0.48	0.15	0.21	0.16	0.13	0.21	0.27	0.39
u(xi)	4.11	6.22	5.37	5.10	5.78	6.15	10.99	6.22	8.89
U(xi)	8.22	12.45	10.74	10.20	11.56	12.30	21.98	12.44	17.43

Table 28: Reported values for NO run 2.

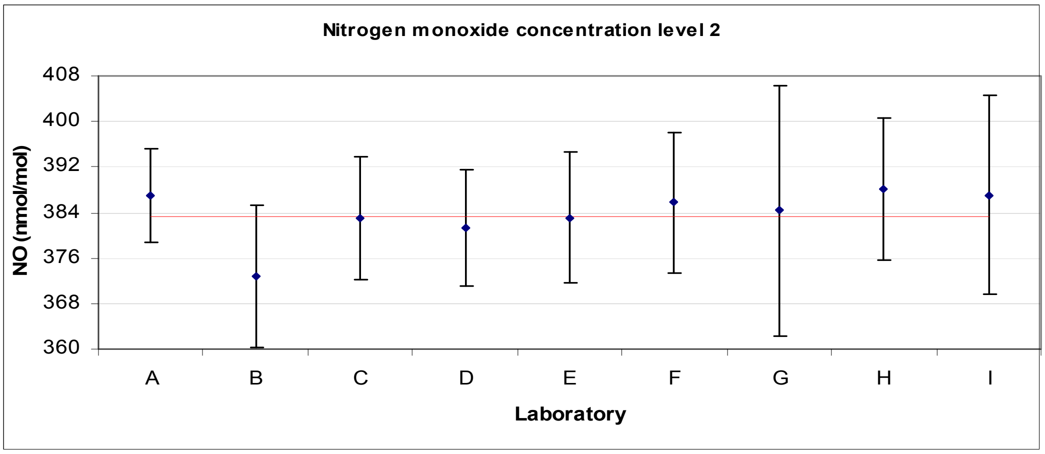

Figure 33: Reported values for NO run 2.

parameter:	NO			all units are nmol/mol					
run:	3			x*: 253.8		s*: 2.0			
	A	B	C	D	E	F	G	H	I
xi,1	253.04	243.14	253.65	251.40	253.17	255.60	254.80	257.83	252.97
xi,2	253.77	243.26	253.87	251.60	253.38	255.91	254.90	258.16	253.26
xi,3	254.14	243.40	254.00	251.91	253.63	255.88	254.90	258.40	253.58
xi	253.65	243.27	253.84	251.64	253.39	255.80	254.87	258.13	253.27
si	0.56	0.13	0.18	0.26	0.23	0.17	0.06	0.29	0.31
u(xi)	2.69	4.21	3.58	3.40	4.05	4.09	7.36	4.13	5.86
U(xi)	5.38	8.43	7.17	6.80	8.10	8.18	14.72	8.26	11.49

Table 29: Reported values for NO run 3.

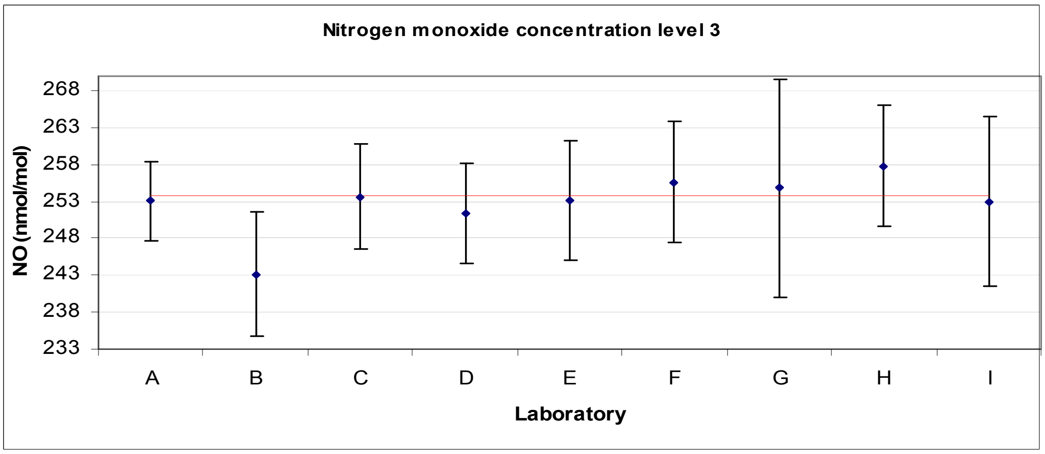

Figure 34: Reported values for NO run 3.

parameter:	NO			all units are	nmol/mol				
run:	4			x*:	154.2	s*:	2.8		
	A	B	C	D	E	F	G	H	I
xi,1	155.61	150.59	154.03	152.99	154.43	155.21	149.00	157.55	156.75
xi,2	155.97	150.58	153.93	152.89	154.13	155.10	148.80	157.63	156.80
xi,3	156.02	150.93	153.92	152.89	154.17	155.16	148.80	157.50	156.82
xi	155.87	150.70	153.96	152.92	154.24	155.16	148.87	157.56	156.79
si	0.22	0.20	0.06	0.06	0.16	0.06	0.12	0.07	0.04
u(xi)	1.63	2.81	2.21	2.10	2.74	2.50	4.27	2.52	3.71
U(xi)	3.26	5.63	4.42	4.20	5.47	5.00	8.54	5.04	7.28

Table 30: Reported values for NO run 4.

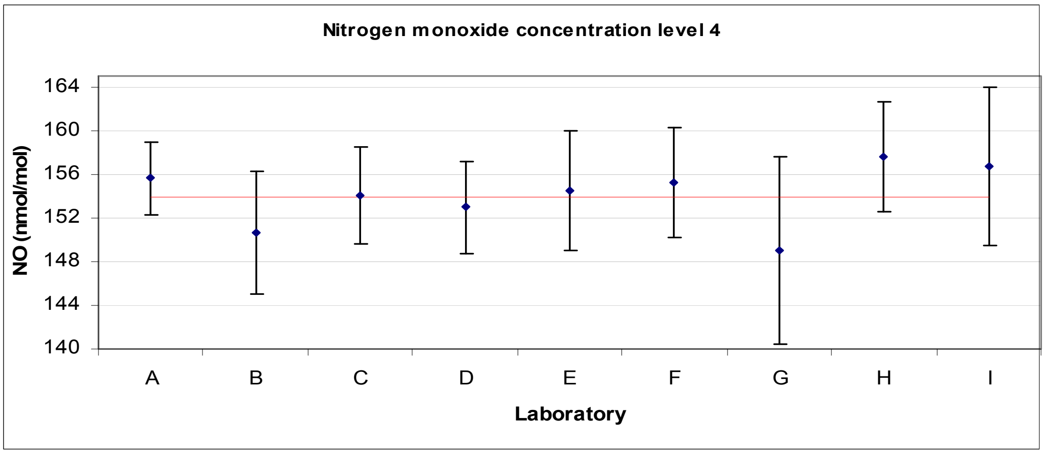

Figure 35: Reported values for NO run 4.

parameter:	NO			all units are	nmol/mol				
run:	5			x*:	153.7	s*:	1.7		
	A	B	C	D	E	F	G	H	I
xi,1	153.51	147.27	154.39	152.79	154.35	155.52	151.70	157.50	153.24
xi,2	153.85	147.13	154.48	152.79	154.44	155.72	151.80	157.51	153.44
xi,3	153.75	146.98	154.62	152.79	154.48	155.66	151.70	157.59	153.41
xi	153.70	147.13	154.50	152.79	154.42	155.63	151.73	157.53	153.36
si	0.18	0.15	0.12	0.00	0.07	0.10	0.06	0.05	0.11
u(xi)	1.60	2.77	2.22	2.10	2.74	2.50	4.35	2.52	3.64
U(xi)	3.20	5.54	4.44	4.20	5.47	5.00	8.70	5.04	7.13

Table 31: Reported values for NO run 5.

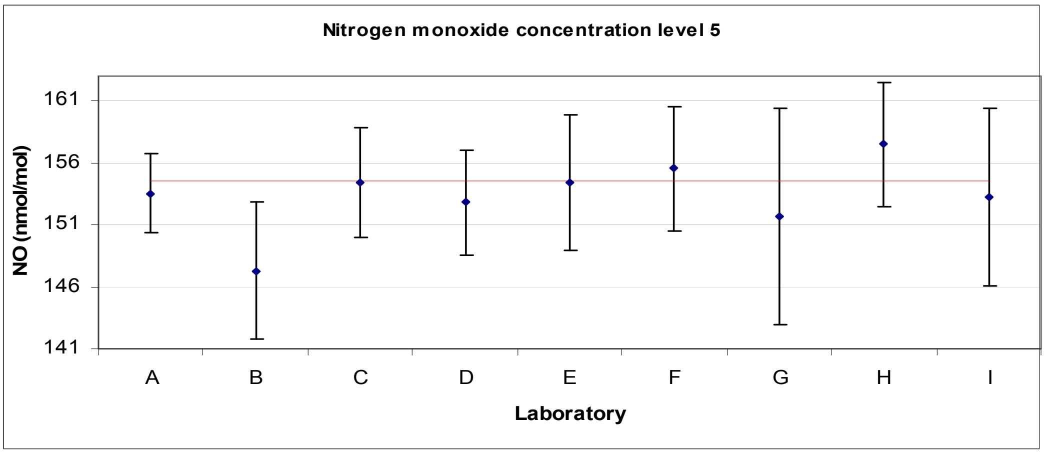

Figure 36: Reported values for NO run 5.

parameter:	NO				all units are nmol/mol				
run:	6			x*:	94.8		s*:	1.9	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	95.99	91.80	94.88	93.90	95.14	95.24	91.30	97.08	96.57
xi,2	96.06	91.80	94.83	93.97	95.22	95.23	91.20	96.95	96.51
xi,3	95.97	91.78	94.87	93.75	95.07	95.24	91.10	96.89	96.45
xi	96.01	91.79	94.86	93.87	95.14	95.24	91.20	96.97	96.51
si	0.05	0.01	0.03	0.11	0.08	0.01	0.10	0.10	0.06
u(xi)	1.02	2.03	1.40	1.20	1.95	1.56	2.63	1.55	2.42
U(xi)	2.04	4.07	2.81	2.40	3.89	3.12	5.26	3.10	4.74

Table 32: Reported values for NO run 6.

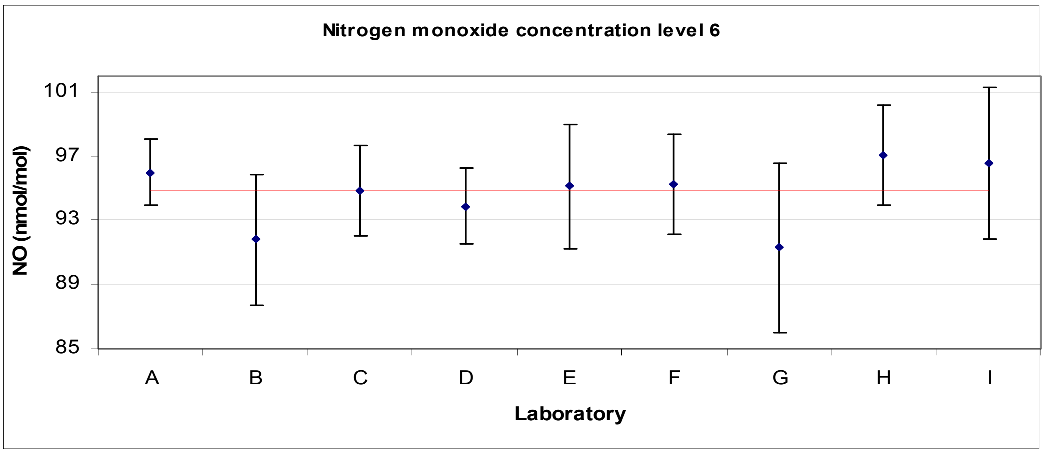

Figure 37: Reported values for NO run 6.

parameter:	NO				all units are nmol/mol				
run:	7			x*:	51.8		s*:	1.6	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	51.52	48.92	52.44	51.60	52.97	52.82	50.10	53.82	51.35
xi,2	51.80	48.84	52.54	51.64	52.99	52.87	50.00	53.87	51.51
xi,3	51.69	48.77	52.49	51.66	53.00	52.89	50.10	53.88	51.52
xi	51.67	48.84	52.49	51.63	52.99	52.86	50.07	53.86	51.46
si	0.14	0.08	0.05	0.03	0.02	0.04	0.06	0.03	0.10
u(xi)	0.52	1.58	0.83	0.74	1.39	0.92	1.45	0.86	1.54
U(xi)	1.05	3.15	1.67	1.50	2.77	1.85	2.90	1.72	3.02

Table 33: Reported values for NO run 7.

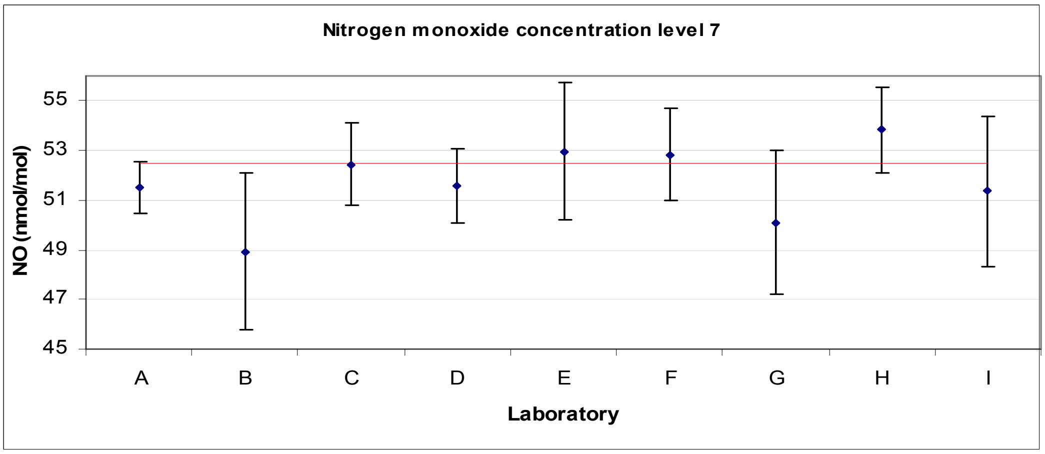

Figure 38: Reported values for NO run 7.

parameter:	NO				all units are nmol/mol			
run:	8			x*:	31.7	s*:	0.9	

	A	B	C	D	E	F	G	H	I
xi,1	31.79	29.57	31.82	31.23	32.53	32.17	29.20	32.91	32.11
xi,2	31.70	29.57	31.78	31.09	32.40	32.16	29.10	32.83	32.13
xi,3	32.07	29.49	31.79	31.07	32.36	32.16	29.10	32.83	32.16
xi	31.85	29.54	31.80	31.13	32.43	32.16	29.13	32.86	32.13
si	0.19	0.05	0.02	0.09	0.09	0.01	0.06	0.05	0.03
u(xi)	0.55	1.44	0.59	0.50	1.12	0.64	0.85	0.53	1.24
U(xi)	1.05	2.89	1.17	1.00	2.23	1.28	1.70	1.06	2.43

Table 34: Reported values for NO run 8.

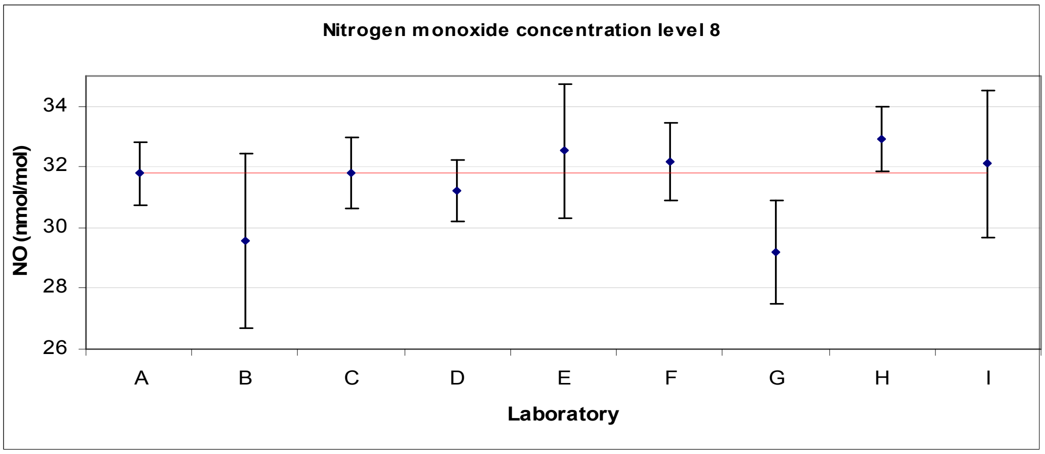

Figure 39: Reported values for NO run 8.

parameter:	NO				all units are nmol/mol			
run:	9			x*:	16.7	s*:	0.8	

	A	B	C	D	E	F	G	H	I
xi,1	16.41	14.71	17.05	16.37	17.89	17.09	16.10	17.54	16.22
xi,2	16.64	14.83	17.09	16.68	17.80	17.10	16.20	17.55	16.30
xi,3	16.34	14.71	17.07	16.70	17.92	17.09	16.10	17.63	16.26
xi	16.46	14.75	17.07	16.58	17.87	17.09	16.13	17.57	16.26
si	0.16	0.07	0.02	0.19	0.06	0.01	0.06	0.05	0.04
u(xi)	0.52	1.37	0.42	0.36	0.92	0.47	0.50	0.28	1.07
U(xi)	1.05	2.75	0.85	0.72	1.84	0.95	1.00	0.56	2.09

Table 35: Reported values for NO run 9.

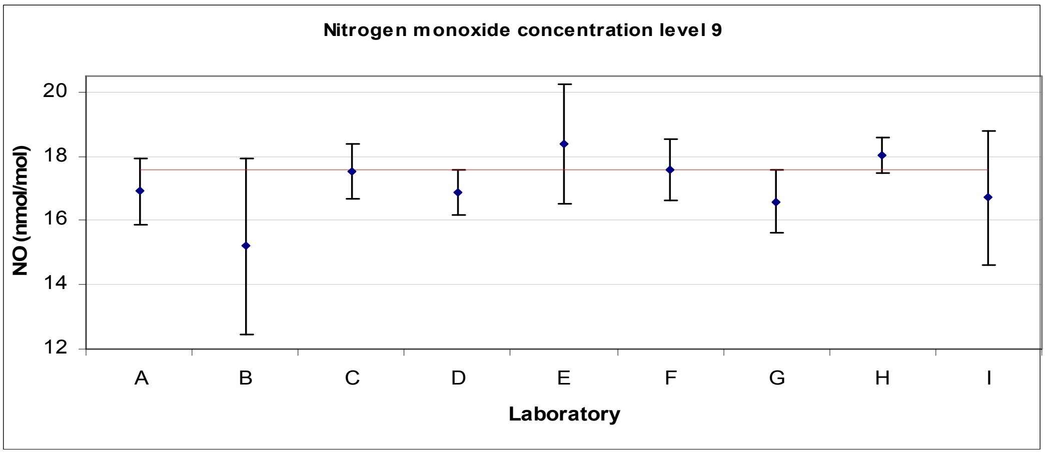

Figure 40: Reported values for NO run 9.

parameter:	NO				all units are nmol/mol				
run:	10				x*:	3.4	s*:	0.5	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	3.57	2.16	3.38	3.09	4.33	3.16	1.90	3.82	3.66
xi,2	3.61	2.15	3.37	3.20	4.43	3.22	1.90	3.78	3.68
xi,3	3.60	2.13	3.35	3.17	4.28	3.20	1.80	3.70	3.62
xi	3.59	2.15	3.37	3.15	4.35	3.19	1.87	3.77	3.65
si	0.02	0.02	0.02	0.06	0.08	0.03	0.06	0.06	0.03
u(xi)	0.52	1.35	0.33	0.31	0.74	0.39	0.18	0.07	1.00
U(xi)	1.05	2.71	0.66	0.62	1.48	0.78	0.36	0.14	1.97

Table 36: Reported values for NO run 10.

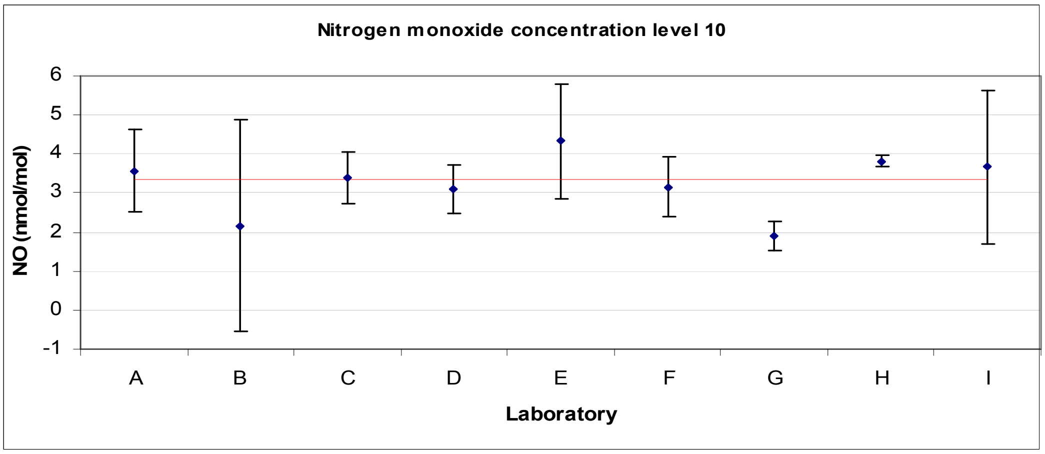

Figure 41: Reported values for NO run 10.

Reported values for NO_2

parameter: NO_2					all units are nmol/mol				
run: 0					x*: 0.0		s*: 0.3		
	A	B	C	D	E	F	G	H	I
xi,1	0.50	-0.02	-0.22	0.04	-0.45	0.01	0.10	-0.15	0.36
u(xi)	0.73	2.39	0.12	0.47	1.01	0.38	0.01	0.00	1.00
U(xi)	1.46	4.78	0.24	0.94	2.01	0.77	0.02	-0.01	1.96

Table 37: Reported values for NO_2 run 0.

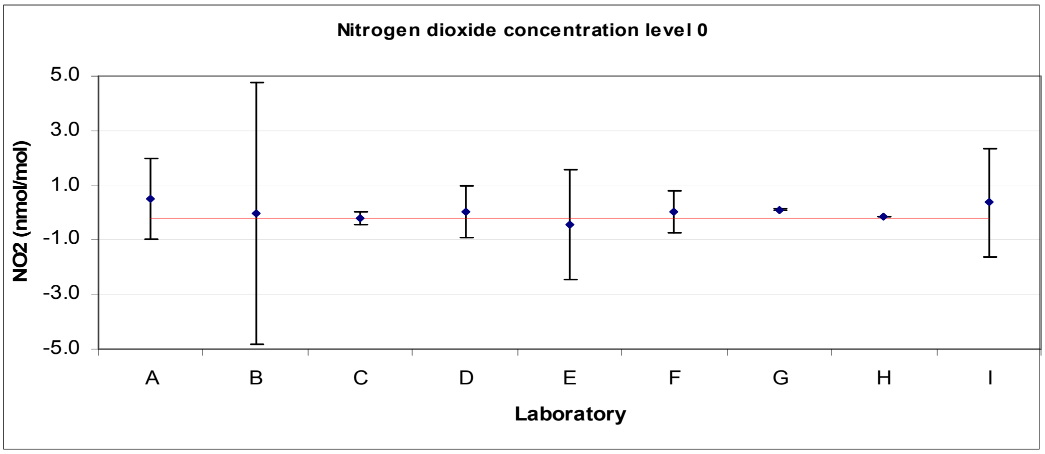

Figure 42: Reported values for NO_2 run 0.

parameter: NO_2					all units are nmol/mol				
run: 1					x*: 2.6		s*: 2.2		
	A	B	C	D	E	F	G	H	I
xi,1	1.18	5.76	3.24	2.14	0.36	3.16		5.09	2.82
xi,2	1.14	5.81	3.34	2.54	0.46	3.06		4.66	2.33
xi,3	0.78	6.69	3.15	2.54	0.50	3.06		4.67	2.98
xi	1.03	6.09	3.24	2.41	0.44	3.09		4.81	2.71
si	0.22	0.52	0.10	0.23	0.07	0.06		0.25	0.34
u(xi)	0.73	10.74	1.09	0.47		0.39		0.18	1.00
U(xi)	1.46	21.48	2.18	0.94		0.78		0.36	1.96

Table 38: Reported values for NO_2 run 1.

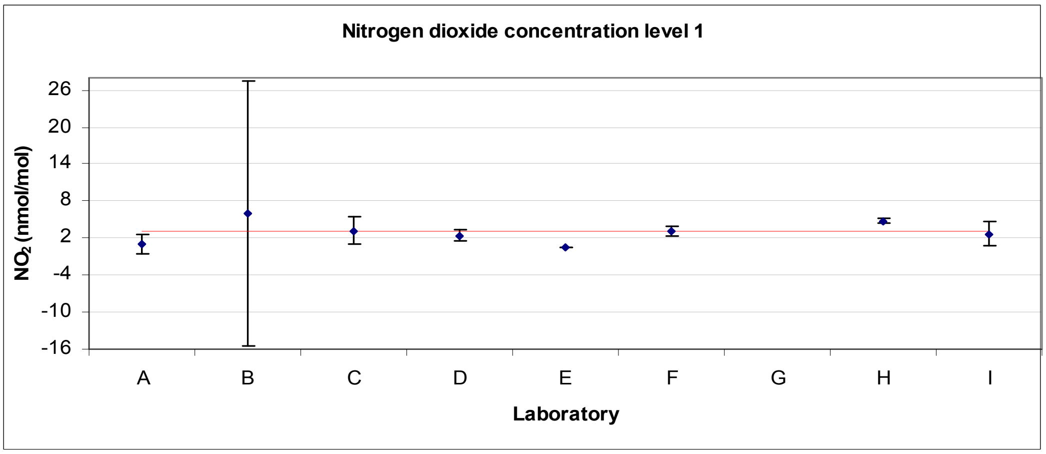

Figure 43: Reported values for NO_2 run 1.

parameter: NO_2					all units are nmol/mol				
	run: 2				x*: 119.0		s*: 3.5		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	117.79	116.42	122.23	120.22	117.17	123.50	118.00	126.38	115.15
xi,2	117.44	115.68	121.92	120.12	116.82	123.39	118.20	126.04	114.51
xi,3	116.82	115.71	121.51	120.12	117.06	123.40	118.20	125.91	114.79
xi	117.35	115.94	121.89	120.15	117.02	123.43	118.13	126.11	114.82
si	0.49	0.42	0.36	0.06	0.18	0.06	0.12	0.24	0.32
u(xi)	1.78	9.16	1.63	2.00	2.13	2.15	3.41	2.90	2.80
U(xi)	3.56	18.33	3.25	4.00	4.25	4.29	6.82	5.80	5.49

Table 39: Reported values for NO_2 run 2.

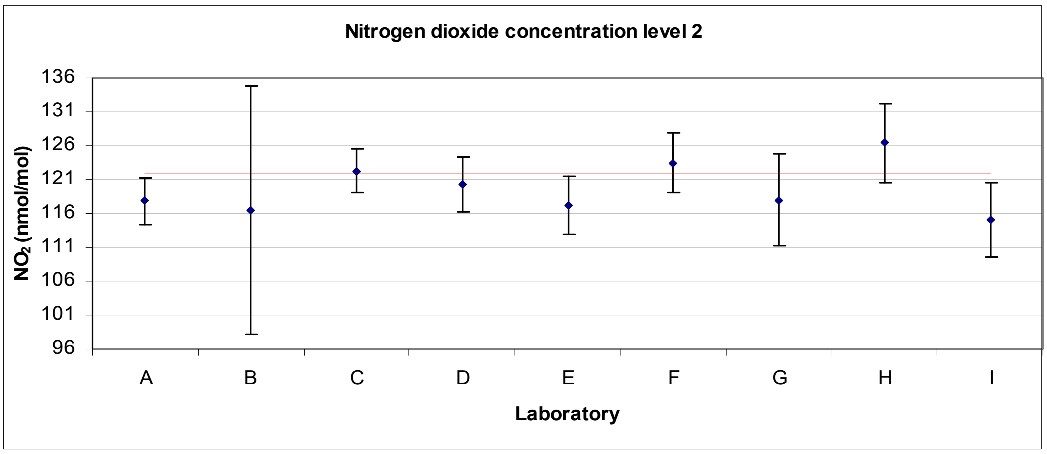

Figure 44: Reported values for NO_2 run 2.

parameter: NO_2					all units are nmol/mol				
	run: 3				x*: 0.9		s*: 1.1		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	-0.03	1.71	1.30	1.21	-0.25	1.30		1.98	1.25
xi,2	-1.23	1.96	1.27	1.21	-0.16	1.22		2.16	0.97
xi,3	-0.70	2.72	1.38	1.31	-0.09	1.22		2.01	0.77
xi	-0.65	2.13	1.32	1.24	-0.17	1.25		2.05	1.00
si	0.60	0.53	0.06	0.06	0.08	0.05		0.10	0.24
u(xi)	0.73	5.33	0.60	0.47		0.38		0.07	1.00
U(xi)	1.46	10.66	1.20	0.94		0.77		0.14	1.96

Table 40: Reported values for NO_2 run 3.

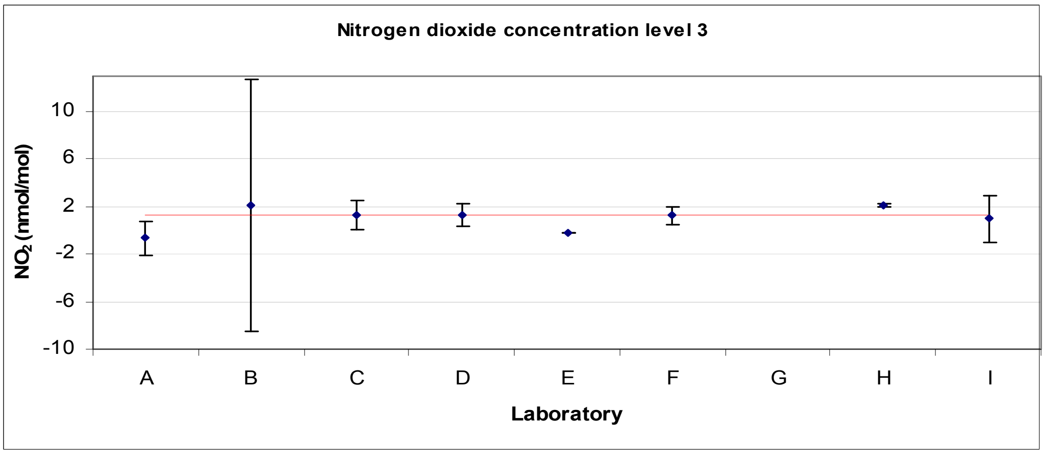

Figure 45: Reported values for NO_2 run 3.

parameter: NO_2 run: 4					all units are nmol/mol x*: 99.9		s*: 3.9		
	A	B	C	D	E	F	G	H	I
xi,1	97.29	94.35	101.21	100.23	98.14	102.51	102.70	105.14	95.72
xi,2	97.69	94.08	101.12	100.33	98.51	102.91	102.10	105.06	95.76
xi,3	97.49	94.37	101.47	100.43	98.53	102.75	102.80	105.30	95.99
xi	97.49	94.27	101.27	100.33	98.39	102.72	102.53	105.17	95.82
si	0.20	0.16	0.18	0.10	0.22	0.20	0.38	0.12	0.15
u(xi)	1.47	4.25	1.25	1.80	1.95	1.79	2.96	2.42	2.40
U(xi)	2.95	8.50	2.50	3.60	3.89	3.59	5.02	4.84	4.71

Table 41: Reported values for NO_2 run 4.

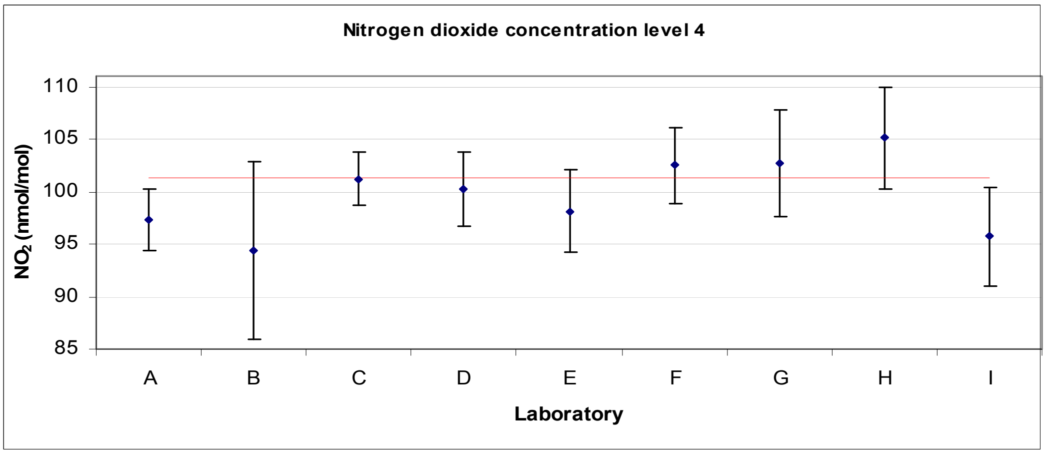

Figure 46: Reported values for NO_2 run 4.

parameter: NO_2 run: 5					all units are nmol/mol x*: 0.1		s*: 0.5		
	A	B	C	D	E	F	G	H	I
xi,1	-0.70	0.95	0.13	0.24	-0.56	0.32		0.70	0.00
xi,2	-1.07	2.02	0.17	0.44	-0.80	0.22		0.74	0.16
xi,3	-0.95	1.80	0.03	0.44	-0.66	0.24		0.55	0.18
xi	-0.91	1.59	0.11	0.37	-0.67	0.26		0.66	0.11
si	0.19	0.57	0.07	0.12	0.12	0.05		0.10	0.10
u(xi)	0.73	3.34	0.47	0.47		0.39		0.06	1.00
U(xi)	1.46	6.68	0.93	0.94		0.77		0.12	1.96

Table 42: Reported values for NO_2 run 5.

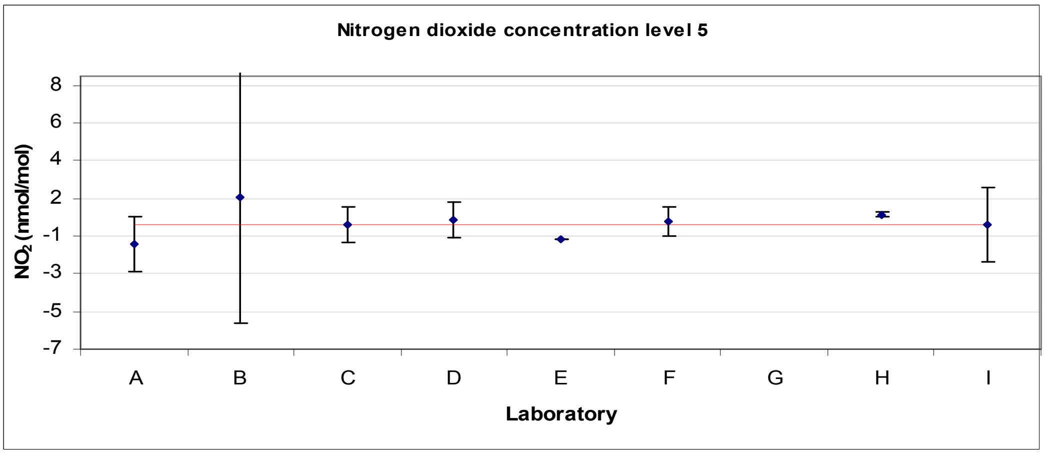

Figure 47: Reported values for NO_2 run 5.

parameter: NO_2				all units are nmol/mol					
run: 6				x*: 58.9		s*: 2.2			
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	57.25	57.08	59.89	59.43	58.03	60.91	59.10	62.23	56.41
xi,2	56.98	56.97	59.91	59.36	58.08	60.98	59.20	62.32	56.43
xi,3	57.40	57.05	59.91	59.48	58.13	60.96	59.30	62.49	56.54
xi	57.21	57.03	59.90	59.42	58.08	60.95	59.20	62.35	56.46
si	0.21	0.06	0.01	0.06	0.05	0.04	0.10	0.13	0.07
u(xi)	0.86	2.74	0.79	1.10	1.56	1.11	1.80	1.44	1.63
U(xi)	1.73	5.49	1.58	2.20	3.12	2.22	3.60	2.88	3.20

Table 43: Reported values for NO_2 run 6.

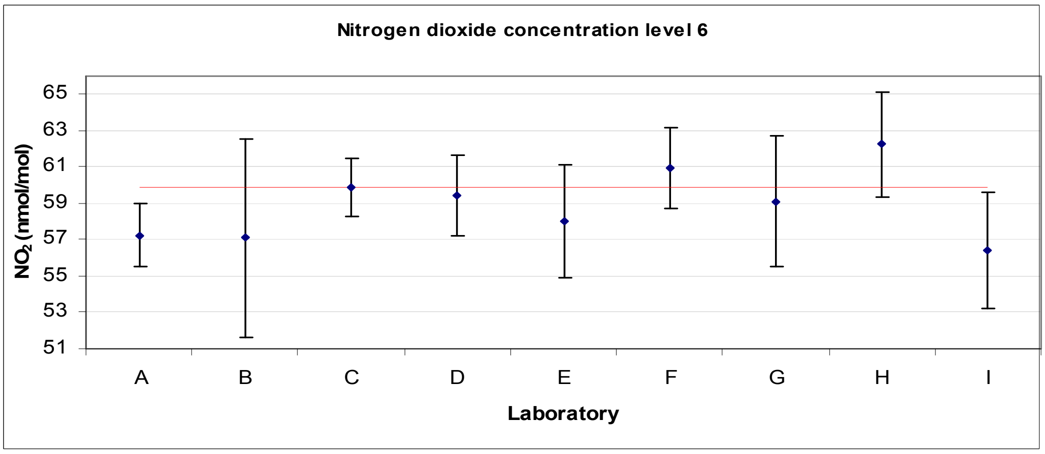

Figure 48: Reported values for NO_2 run 6.

parameter: NO_2				all units are nmol/mol					
run: 7				x*: 0.0		s*: 0.2			
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	-0.48	0.52	-0.15	0.20	-0.44	0.03		0.15	-0.09
xi,2	-0.50	0.69	-0.15	0.15	-0.53	0.01		0.03	-0.04
xi,3	-0.28	0.68	-0.13	0.18	-0.55	0.01		-0.02	-0.16
xi	-0.42	0.63	-0.14	0.18	-0.51	0.02		0.05	-0.10
si	0.12	0.10	0.01	0.03	0.06	0.01		0.09	0.06
u(xi)	0.73	1.65	0.26	0.47		0.39		0.05	1.00
U(xi)	1.46	3.30	0.52	0.94		0.77		0.10	1.96

Table 44: Reported values for NO_2 run 7.

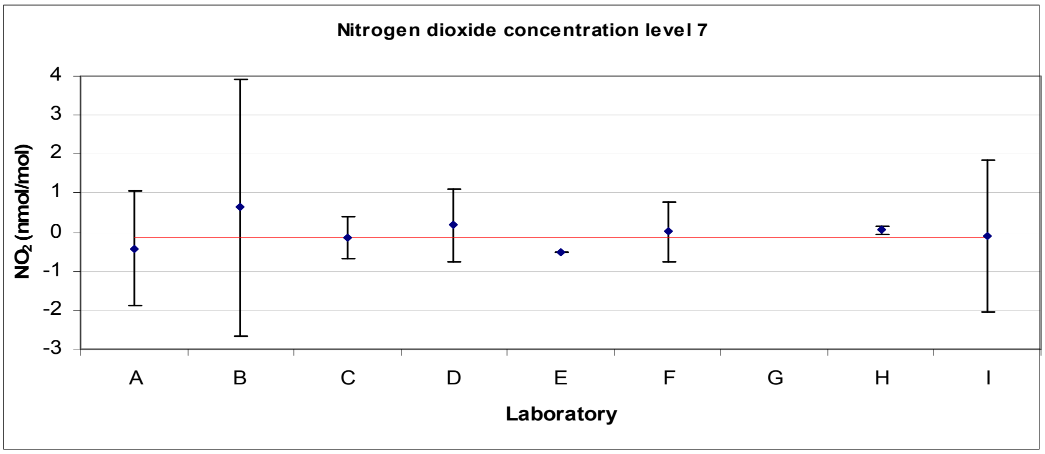

Figure 49: Reported values for NO_2 run 7.

	parameter: NO_2				all units are nmol/mol				
	run: 8				x*: 20.2		s*: 0.9		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	19.51	19.64	20.54	20.54	19.74	21.01	20.20	21.46	19.20
xi,2	19.42	19.59	20.70	20.66	19.77	21.02	20.20	21.53	19.17
xi,3	19.47	19.53	20.70	20.58	19.81	21.01	20.30	21.42	19.22
xi	19.47	19.59	20.65	20.59	19.77	21.01	20.23	21.47	19.20
si	0.05	0.06	0.09	0.06	0.04	0.01	0.06	0.06	0.03
u(xi)	0.73	1.69	0.35	0.58	1.19	0.52	0.62	0.49	1.09
U(xi)	1.46	3.38	0.70	1.20	2.38	1.06	1.24	0.98	2.14

Table 45: Reported values for NO_2 run 8.

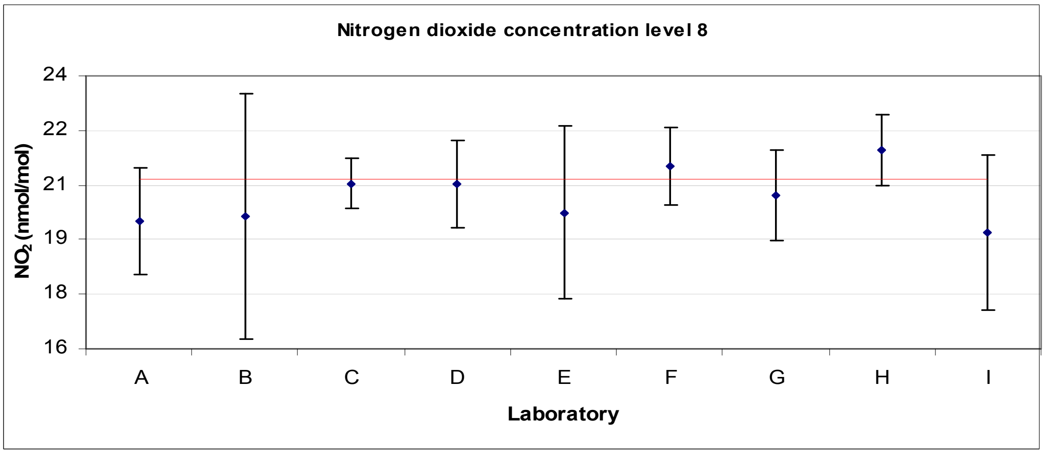

Figure 50: Reported values for NO_2 run 8.

	parameter: NO_2				all units are nmol/mol				
	run: 9				x*: -0.1		s*: 0.1		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	-0.13	0.31	-0.12	0.13	-0.48	0.01		-0.04	-0.01
xi,2	-0.42	0.39	-0.15	0.01	-0.43	0.01		-0.10	-0.08
xi,3	0.01	0.43	-0.15	0.10	-0.55	0.01		-0.17	-0.09
xi	-0.18	0.38	-0.14	0.08	-0.49	0.01		-0.10	-0.06
si	0.22	0.06	0.02	0.06	0.06	0.00		0.07	0.04
u(xi)	0.73	1.64	0.20	0.47		0.39		0.04	1.00
U(xi)	1.46	3.27	0.39	0.94		0.77		0.08	1.96

Table 46: Reported values for NO_2 run 9.

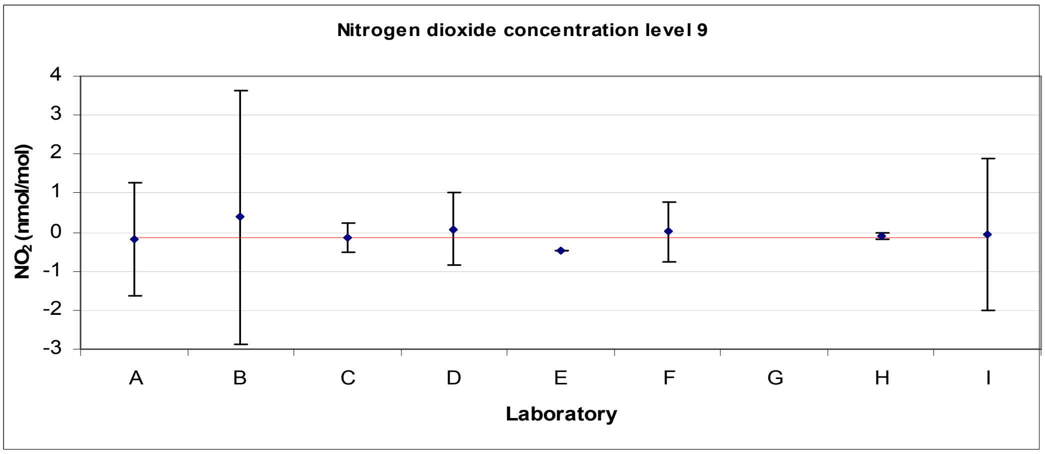

Figure 51: Reported values for NO_2 run 9.

parameter: NO_2					all units are nmol/mol				
run: 10					x*: 13.4		s*: 0.7		
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi,1	12.75	12.83	13.46	13.56	12.84	14.15	14.20	13.92	12.49
xi,2	12.74	12.97	13.51	13.56	12.88	14.14	14.30	13.94	12.50
xi,3	12.87	13.01	13.58	13.59	12.96	14.12	14.50	14.01	12.56
xi	12.79	12.94	13.52	13.57	12.89	14.14	14.33	13.96	12.52
si	0.07	0.10	0.06	0.02	0.06	0.02	0.15	0.05	0.04
u(xi)	0.73	1.68	0.23	0.50	1.13	0.46	0.44	0.32	1.04
U(xi)	1.46	3.36	0.46	1.00	2.25	0.91	0.88	0.64	2.04

Table 47: Reported values for NO_2 run 10.

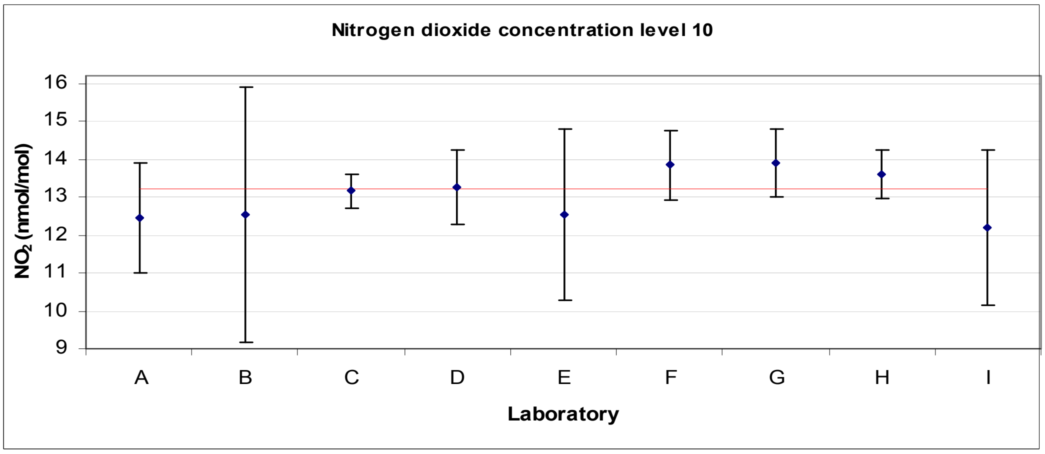

Figure 52: Reported values for NO_2 run 10.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken by ERLAP the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [2], [3], [4] and [5] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [14], [15] and [16]. The precision experiment has involved a total of eight laboratories, the actual number of labs (p_j) varying from run to run (Table 48). Six concentration levels were tested, for O_3, CO, SO_2 and NO_2, and eleven for NO. Outlier tests were performed and results are reported in Annex D.

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using equation 8 [16]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not been exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_r \qquad (8)$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using equation 9 [16]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, which should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_R \qquad (9)$$

The repeatability standard deviation was evaluated with ($p_j \cdot (3-1)$) degrees of freedom (ν) and reproducibility standard deviation with (p_j-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are reported in Table 48.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	0-5	8	2.120	2.365
NO	1,3	7	2.145	2.447
NO	0,2,4-10	8	2.120	2.365
NO_2	1,3,5,7,9	7	2.145	2.447
NO_2	0,2,4,6,8,10	8	2.120	2.365
O_3	3	7	2.145	2.447
O_3	0-2,4,5	8	2.120	2.365
SO_2	5	7	2.145	2.447
SO_2	0-4	8	2.120	2.365

Table 48: Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

The repeatability (r) and reproducibility (R) limits of measurement methods are presented from Table 50 to Table 53 and from Figure 54 to Figure 57. It is also reported the 'reproducibility from common criteria (R(from σ_p))' calculated by substituting s_R in equation 9 with a 'standard deviation for proficiency assessment' (Table 4). Comparison between R and R(from σ_p) serves to indicate that σ_p is realistic ([13] 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is appropriate for σ_p.

SO_2 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.0		1.0	
3.0	0.2	1.0	
7.4	0.5	3.1	
19.0	0.3	4.4	
48.1	0.3	6.3	
135.5	0.7	15.5	11.4%

Table 49: The R and r of SO_2 standard measurement method.

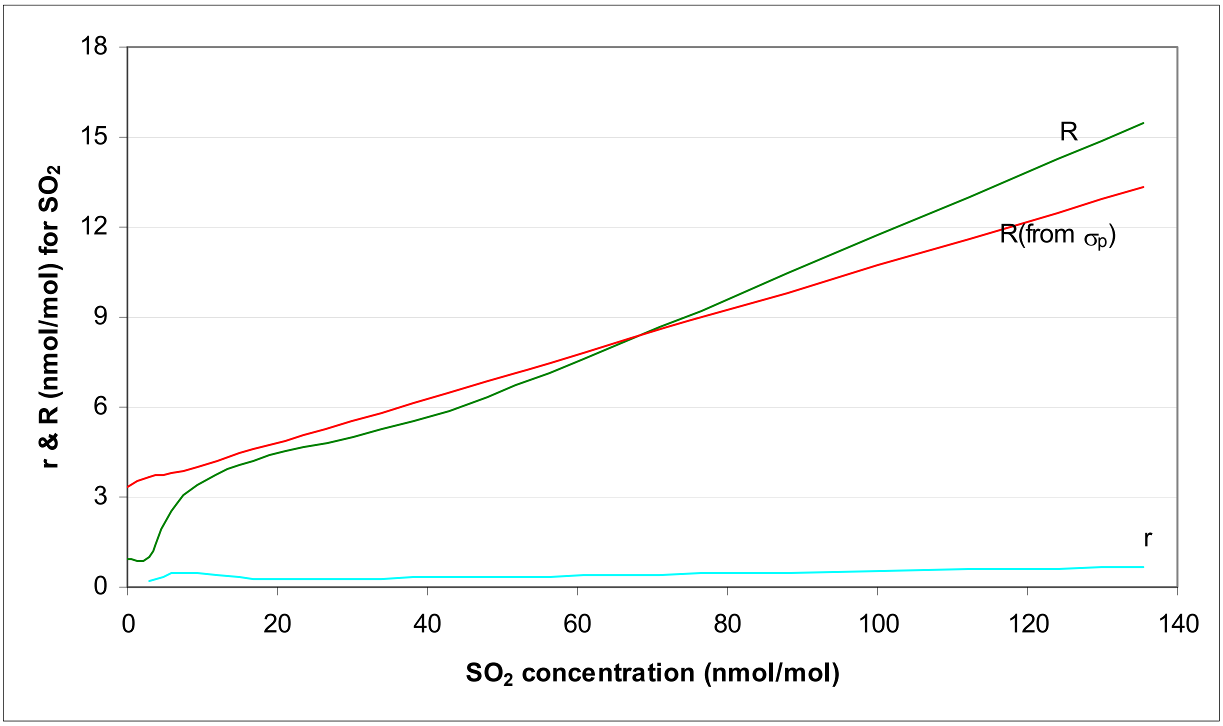

Figure 53: The R and r of SO_2 standard measurement method as a function of concentration.

CO data (µmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
-0.003		0.092	
1.014	0.009	0.225	
2.008	0.012	0.359	
4.283	0.019	0.414	
5.938	0.012	0.49	
8.455	0.026	0.669	7.9%

Table 50: The R and r of CO standard measurement method.

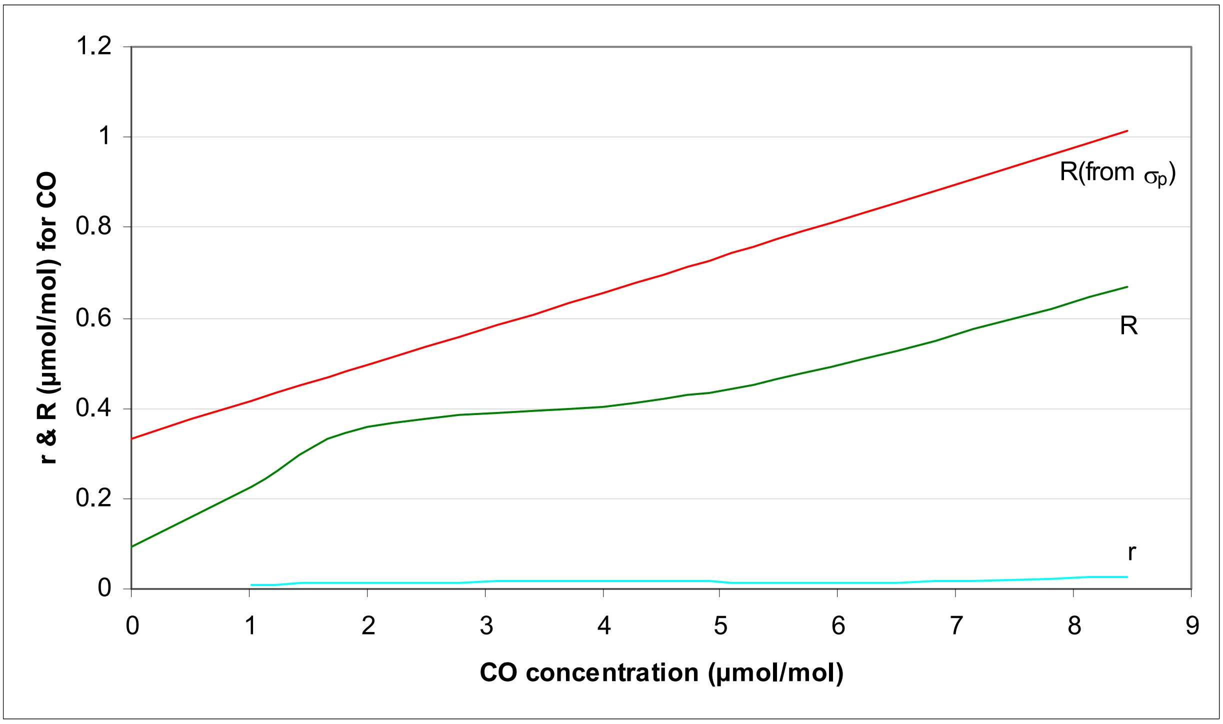

Figure 54: The R and r of CO standard measurement method as a function of concentration.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.0		1.2	
14.1	0.2	2.2	
21.2	0.1	3.2	
60.0	0.1	2.4	
101.3	1.3	9.1	
120.0	1.6	10.7	8.9%

Table 51: The R and r of O_3 standard measurement method.

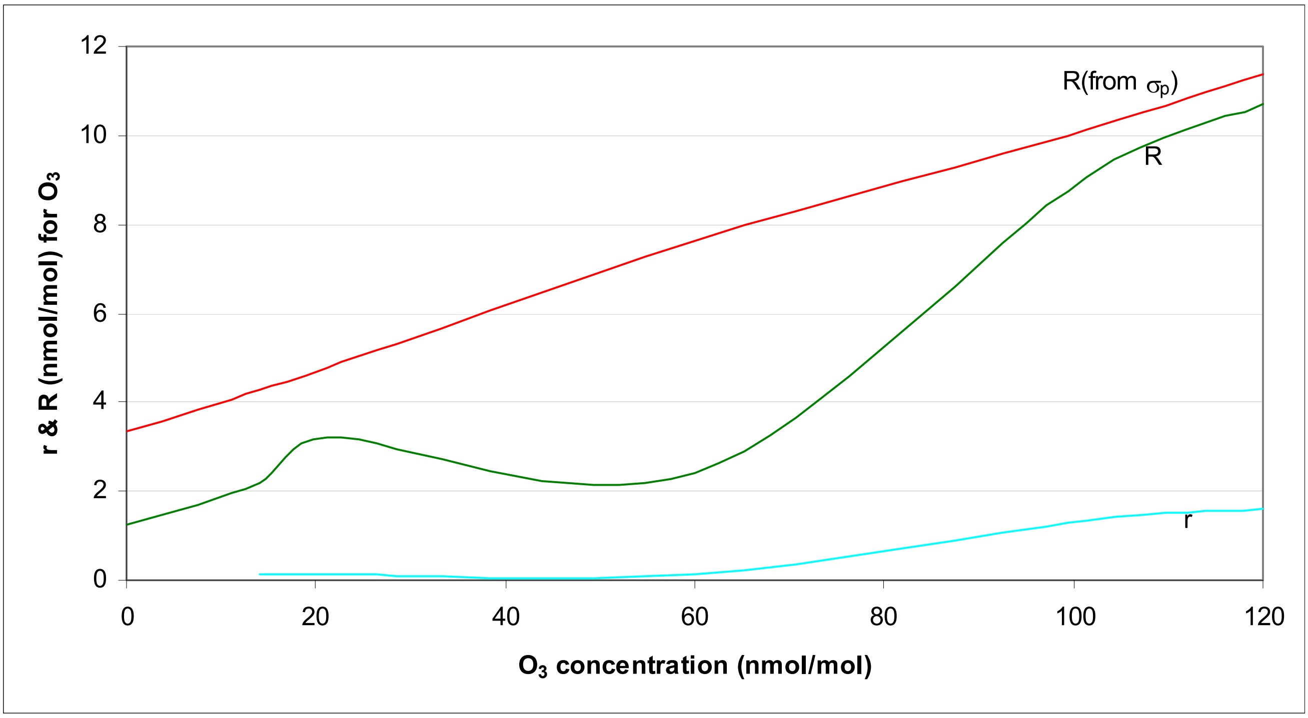

Figure 55: The R and r of O_3 standard measurement method as a function of concentration.

NO data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2		2.6	
3.2	0.1	2.8	
16.6	0.3	3.3	
31.4	0.3	4.6	
51.7	0.2	5.4	
94.6	0.2	7.1	
153.3	0.3	10.2	
154.0	0.4	10.1	
254.4	0.9	7.3	
384.0	1.1	16.5	
503.2	1.4	9.9	2.0%

Table 52: The R and r of NO standard measurement method.

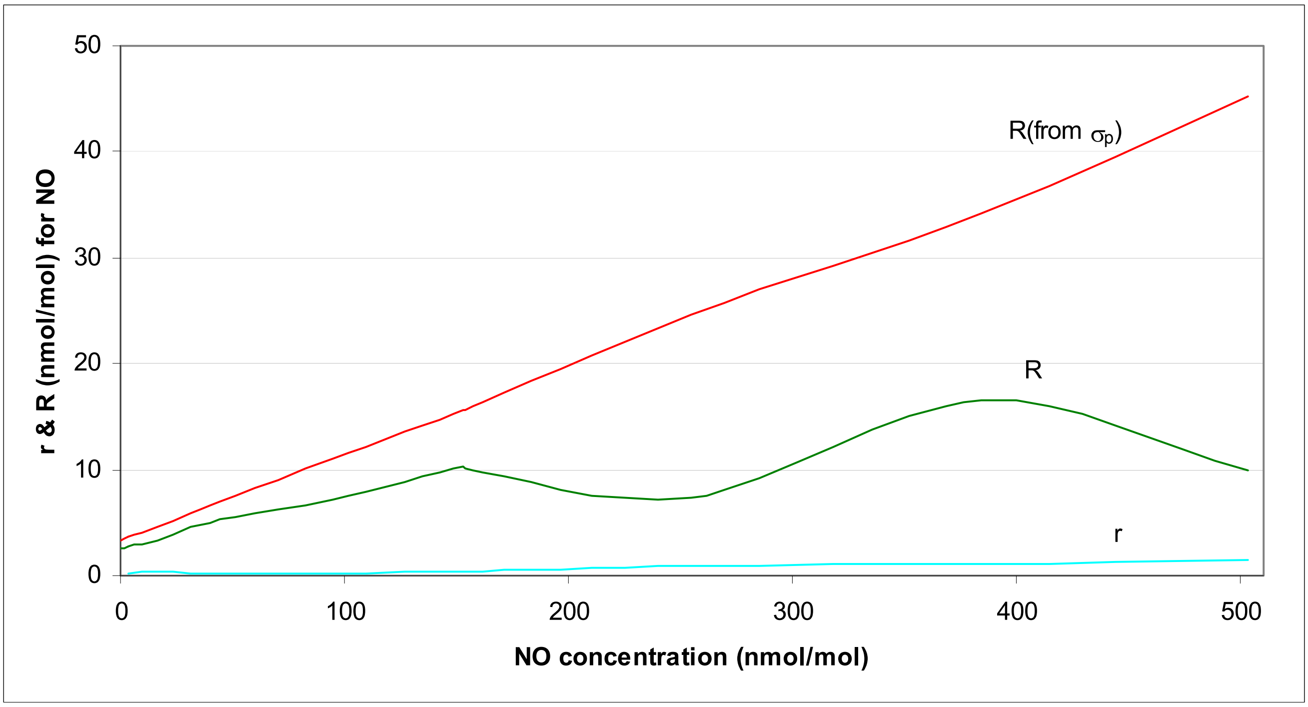

Figure 56: The R and r of NO standard measurement method as a function of concentration.

The reproducibility and repeatability of NO_2 measurements are dependant on both NO and NO_2 concentrations. In Table 53 both concentrations are given and in Figure 57, R and r are plotted as functions of NO_2 concentration.

NO_2 data (nmol/mol) without outliers				
NO	NO_2	NO_2		
group average	group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2	0.0		1.0	
3.2	13.4	0.2	2.3	
16.6	-0.1	0.3	0.9	
31.4	20.2	0.1	2.7	
51.7	0.0	0.2	1.3	
94.6	58.8	0.3	6.9	
153.3	0.2	0.7	3.0	
154.0	99.6	0.6	12.6	
254.4	1.0	1.0	3.7	
384.0	119.1	0.8	13.0	10.9%
503.2	2.9	0.9	6.9	

Table 53: The R and r of NO_2 standard measurement method.

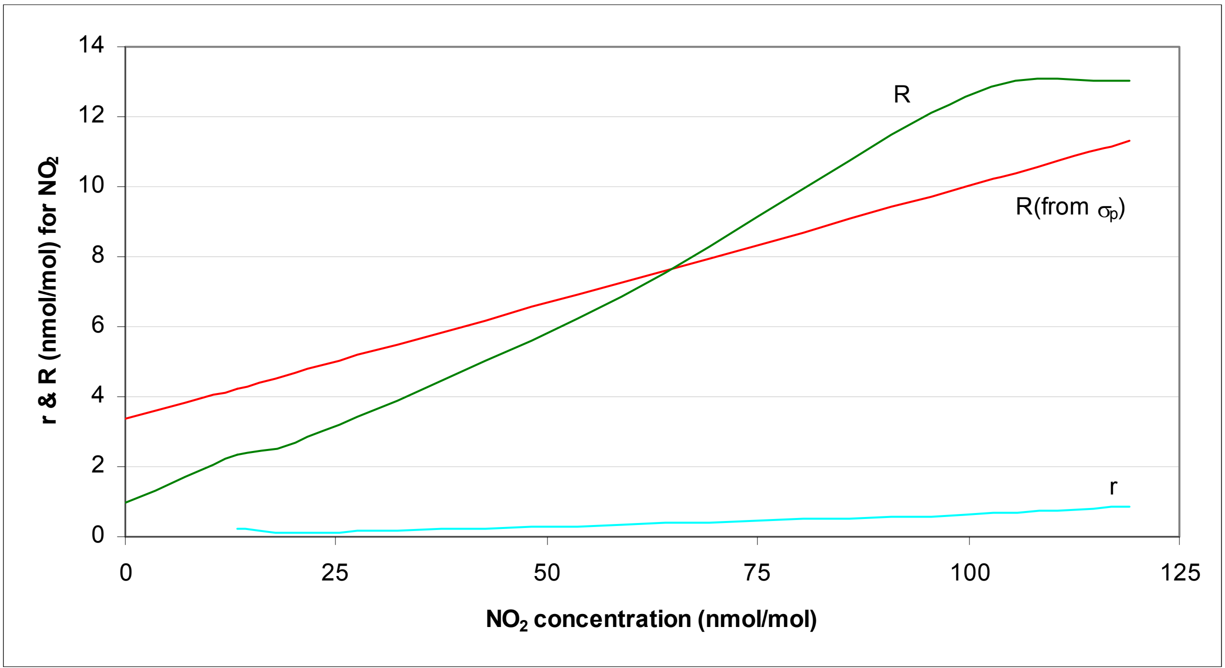

Figure 57: The R and r of NO_2 standard measurement method as a function of concentration.

Annex D. The scrutiny of results for consistency and outlier test

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures. For that reason a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or calculation, wrong averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure were carried out tests for data consistency and statistical outliers as described in ISO 5725-2. Then laboratories showing some form of statistical inconsistency were requested to investigate the cause of discrepancies. Despite laboratories were allowed to correct their results in case of identification of exceptional errors none did so. Subsequently data were considered definitive and "Grubb's one outlying observation test" was performed. For runs where outliers were detected outliers were removed and "Grubb's one outlying observation test" was repeated until no more outliers were observed. Statistical outliers obtained at this stage are not considered as due to extraordinary errors but due to significant difference in participant's standard operating procedure. These "genuine" statistical outliers are presented in table below:

parameter	run	laboratory	measured value	failing test	confidence level
NO	3	B	243.267	G1 minimum	1%, 5%
NO	1	B	482.4	G1 minimum	1%, 5%
SO2	5	H	1.107	G1 minimum	1%, 5%
O3	3	E	63.987	G1 maximum	1%, 5%

Table 54: "Genuine" statistical outliers according to Grubb's one outlying observation test.

The precision of standardized measurement methods reported in Annex C are calculated using the database without outliers.

European Commission

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Abstract

From the 19th to the 22nd of October 2009 in Ispra (IT), 8 Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met at an interlaboratory comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, CO, NO, NO_2 and O_3).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

On the basis of criteria imposed by the European Commission, 85% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 14% of the results had good measured values, but the reported uncertainties were either too high (6%) or too small (8%).

The comparability of results among AQUILA participants is satisfactory for O_3, CO and NO measurement methods. This is not the case for SO_2 and NO_2 which comparability in the present exercise is not satisfactory with respect to the settled quality criteria.

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